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REMOVAL AND RECOVERY OF FLUOBORATES AND METAL IONS FROM ELECTROPLATING WASTEWATER

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16. ABSTRACT

Two separate methods for the treatment of fluoborate wastewater from the electroplating of tin, solder, copper and nickel stripping were investigated. These involved specific ion flotation and electrodialysis to treat dilute waste streams from single tank rinsing or concentrated wastewaters from counter-current or series rinsing, respectively.

The fluoborate ion was found to bind with an alkylamine acetate by displacement of the acetate group and can be removed from dilute waste stream either by air flotation or ultrafiltration. Ultrafiltration provided greater rates of removal than air flotation. The surfactant can be recovered for reuse by electrolysis.

A new high density low porosity graphite anode that is resistant to the corrosive properties of fluoboric acid electrolyte was developed for electrodialysis treatment of the tin, solder and copper fluoborate containing wastewaters. Fluoboric acid electrolyte was used to prevent contamination of the products with sulfate ion. Recoveries of the metal ions were in excess of 90% with the stannous ion being preferentially concentrated in the product and with the stannic ion remaining preferentially in the feed. In general, recoveries of the fluoborate ions were in excess of 80%.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes a laboratory process to remove and recover fluoborates and metals from plating rinsewaters. Several methods were investigated including specific ion flotation, ultrafiltration, electrolysis, and electrodialysis. The results indicate that each method has value depending on the particular requirements in any specific case. This report will be useful to EPA's regulatory program (Effluent Guidelines Division) and to the industry itself in arriving at meaningful and achievable discharge levels. For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The study conducted at the New Jersey Institute of Technology, Newark, New Jersey was concerned with development of two separate methods for treatment of fluoborate-containing wastewater from electroplating of tin, solder, copper and nickel stripping.

The first method was based on the specific ion flotation principle which involves the removal of specific ions from dilute wastewater through binding with a surfactant, followed by flotation or ultrafiltration. This part of the investigation involved the evaluation of structurally different commercially available surfactants to determine the type, structure, mechanism and conditions which govern the formation of a fluoborate-surfactant complex. Also, air flotation and ultrafiltration were evaluated for removal of the complex from the wastewater. Methods for recovery of the surfactant were examined.

The fluoborate was found to bind with a commercially available alkylamine acetate type surfactant which reduces the fluoborate concentration in rinse wastewaters from 100 mg/l of fluoborate to 7-15 mg/l of fluoborate. Actual plating operation rinse wastewaters containing 100 mg/l of fluoborate were used in the study. Ultrafiltration followed by electrolysis provided the shortest treatment time with recovery of the surfactant.

The second method was electrodialysis. Here the major effort was to find a suitable anode. Electrodialysis was found feasible for treatment

of wastestreams containing plating chemical concentrations $\geq$ 1000 mg/l using a high density low porosity graphite anode. Electrodialysis can reduce the plating chemical concentrations in the wastestreams to about 100 mg/l.

The specific ion flotation process either used separately or in the combination with electrodialysis can be useful and effective for closed loop treatment of fluoborate-containing wastewaters from electroplating operations. Reagent recovery in specific ion flotation and fluoborate and metals recoveries in electrodialysis can be achieved in addition to pollution control. However, both methods need further development to make them commercially suitable for treatment of fluoborate-containing wastestreams.

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CONTENTS

		Page
	FOREWORD	iii
	ABSTRACT	iv
	CONTENTS	vi
	FIGURES	viii
	TABLES	x
I.	INTRODUCTION	1
	Ion Flotation	4
	Electrodialysis	6
II.	CONCLUSIONS	10
	Specific Ion Flotation	10
	Electrodialysis	11
III.	RECOMMENDATIONS	13
IV.	EXPERIMENTAL	15
	Ion Flotation	15
	Surfactants	15
	Equipment and Procedures	16
	Fluoborate Analysis	19
	Micelle Formation	19
	Ultrafiltration	19
	Simple Cell	19
	High Volume Cassette	22

Page

Breaking the Fluoborate-Surfactant Complex 25

Addition of Excess Acetic Acid 25

Electrolysis 25

Electrodialysis 27

V. RESULTS AND DISCUSSION 33

Ion Flotation 33

Factors Influencing the Removal of Fluoborate by the Surfactant 34

Process Parameters 44

Removal of Fluoborate from Plating Rinse-Waters 45

Recovery of Surfactant 47

Ultrafiltration 47

Electrodialysis 52

Evaluation of Different Types of Anodes 54

Electrodialysis Result 57

Treatment of Tin Fluoborate Rinse-Waters 57

Treatment of Solder Fluoborate Rinse-Waters 61

Treatment of Copper Fluoborate Rinse-Waters 69

Rates of Mass Transfer 75

Analysis of Electrolyte 76

VI. REFERENCES 78

FIGURES

Number		Page
1	A Schematic of A Simple Electrodialysis Cell	7
2	Flotation Apparatus	17
3	Schematic of A Simple Ultrafiltration Cell	20
4	Single Pass Flow System	23
5	Recirculating Flow System	24
6	Schematic of Electrolysis Set-Up	26
7	Schematic of an Electrodialysis Stack	28
8	Spacer on Graphite Anode to Define S Shaped Flow Pattern .	30
9	Electrodialysis Unit Feed Reservoir and Electrolyte Reservoir	31
10	Treatment of Dilute Sodium Fluoborate Solution with Armac C	35
11	Fluoborate Removal from Solder Rinse-Water Dependence on Surfactant Molecular Size	41
12	Fluoborate Removal from Solder Rinse-Water Dependence on Surfactant Degree of Saturation	42
13	Time Reaction of Fluoborate with Surfactant	43
14	Removal of Fluoborate from Plating Bath Rinse-Waters Using Armac T	46
15	Electrolysis of Surfactant Fluoborate Concentrated Solution from Treatment of Solder Bath Rinse-Water	49

Number		Page
16	Photograph of Corroded Platinized Titanium Anode	53
17	Photograph of Corroded Nickel Anode	56
18	Electrodialysis Treatment of Tin Fluoborate Rinse-Waters, Feed Cation Concentration	58
19	Treatment of Tin Fluoborate Rinse-Waters, Feed Anion Concentration	60
20	Electrodialysis Treatment of Tin Fluoborate Rinse-Water, Product Cation Concentration	62
21	Electrodialysis Treatment of Tin Fluoborate Rinse-Water, Product Anion Concentration	63
22	Electrodialysis Treatment of Solder Fluoborate Rinse-Waters, Feed Cation Concentration	66
23	Electrodialysis Treatment of Solder Fluoborate Rinse-Waters, Feed Anion Concentration	67
24	Electrodialysis Treatment of Solder Fluoborate Rinse-Waters, Product Ion Concentration	68
25	Electrodialysis Treatment of Copper Fluoborate Rinse-Waters, Feed Anion Concentration	72
26	Electrodialysis Treatment of Copper Fluoborate Rinse-Waters, Feed Anion Concentration	73
27	Electrodialysis Treatment of Copper Fluoborate Rinse-Waters, Product Ion Concentration	74

TABLES

Number		Page
1	Effects of pH Removal on Fluoborate Ion	37
2	Fluoborate Removal Using Stepwise Addition of Armac C Surfactant to Sodium Fluoborate	39
3	Removal of Surfactant with Low Through-Put Ultrafiltration Experiment	50
4	Results of Recycled Retentate Experiment, Millipore Cassette	51
5	Changes in Percent Stannous Cation in the Feed and Product with Time During the Electrodialysis Treatment of Tin Fluoborate Rinse-Water	64
6	Changes in the Percent Stannous Ion in Feed and Product with Time During the Electrodialysis Treatment of Solder Fluoborate Rinse-Water	70
7	Rate of Mass Transport of Cations and Fluoborate from Tin, Solder, Copper Fluoborate Rinse-Water	77

I. INTRODUCTION

A recognition of the detrimental effects of industrial pollution on our environment has surfaced in recent years. Along with this awareness came federal regulations calling for reduction of industrial discharges into the environment. The metal finishing industry is an example of an industry, which will need to develop new technology in order to meet the discharge requirements under these regulations.

The metal finishing industry in the United States includes approximately twenty thousand facilities, the majority of which are associated with the automotive, electronic and jewelry industries. These facilities encompass both job-and captive-shops. The major operations performed at metal finishing facilities include cleaning and pickling, annealing, case hardening, polishing, buffing, immersion plating, electroplating, phosphating, conversion coating, oxidizing, painting, electropainting and anodizing.

The wastewater produced in metal finishing operations is mainly generated in two ways. Concentrated wastes come from the dumping of solutions which have become used or fouled. This is especially true of cleaning, stripping, passivating and anodizing solutions. The dilute wastes, which are the larger volume wastes, come from the rinse-waters. These rinses wash off the process solution that has adhered to the surface or was entrapped in crevices due to the shape of the processed piece.

Presently, the most common used procedure for treating metal finishing wastewaters include the following operations:

. Separation of Oil and Grease

. Oxidative Destruction of Cyanides

. Reduction of Chromates

. Neutralization of Acids and Alkalies

. Precipitation of Metal Hydroxides

. Disposal of Sludge

Problems arise mainly with the disposal of sludge because the precipitates present a potential leaching problem when they are disposed of on land. Alternatives to the precipitation process is the recovery and recycle of wastes from their point of generation, or the substitution of toxic process chemicals with less objectionable ones.

Among the more attractive recovery techniques are reverse osmosis, ion exchange, evaporation, ultrafiltration and electrodialysis. In specific areas, these processes have been applied to the recovery of metals from plating rinse-waters, or the concentration of the rinse-waters for the reuse in the plating bath (1).

Substitution of process chemicals is practical only when the replacement does not compromise the quality of the finished product. One such substition is the use of fluoborate to replace cyanides as a conducting salt in plating baths. Fluoborate has been found to be an excellent carrier ion which gives a uniform, bright, well-thrown covering. Also, fluoborate is much less toxic than cyanide, and therefore, provides for a safer plating room. For these reasons, many platers of cadmium, zinc, tin, lead, solder, copper, nickel and iron are replacing their cyanide baths with fluoborate baths.

Commercial fluoborate solutions are presently available for the plating of copper, indium, iron, lead, nickel, tin and their alloys. Also, fluoboric

acid is used in various pretreatment operations, such as stripping and cleaning. The concentration of these rinse-waters is variable, depending upon the rinsing technique which is employed. Dilute rinses would be typical of single tank rinsing, while the concentrated rinse-water would be attributed to multiple tank countercurrent or series rinsing.

The fluoborate ion is an ion in which boron is covalently saturated by fluorine. This ion forms salts in which there is a true cation with no covalent bonding to the anion. Fluoborate is a very small, tightly bound tetrahedron with a uniform charge. It apparently does not polarize (2).

Fluoborate by itself is relatively non-hazardous. However, it will hydrolize (3) in water yielding boric acid and fluoride in accordance with the following equilibrium reaction:

$$HBF_4 + 3H_2O \rightleftharpoons B(OH)_3 + 4HF$$

The presence of this resulting fluoride in our receiving waters is undesirable.

There are presently no specific discharge limitations on fluoborate. However, when a wastestream is analyzed for fluoride by the approved method (Bellack Distillation), any fluoborate present will be hydrolized yielding inflated fluoride concentrations. For each fluoborate ion present in a sample the test will show four fluoride ions. This gives a false indication of fluoride concentration and can show a National Pollution Discharge Elimination System Permit (NPDES) violation where none exists.

Few processes are known for the removal of fluoborate from plating rinse-waters. It is a small tight molecule and is not easily rejected by membrane processes such as reverse osmosis. Presently, there is no known ion exchange resin which will efficiently remove fluoborate from solution. Battele

Memorial Institute in their January 1974 draft of the Development Document for Limitations for Electroplating Point Sources, suggested the hydrolysis of the fluoborate to fluoride, followed by lime precipitation as a possible treatment. This however, results in the production of a sludge that must be disposed in secure landfills.

Vaccum evaporation is currently being used as a means of recycling stannous fluoborate rinse waters back into the plating tank as make-up solution. Although it provides a closed-loop treatment system, problems such as precipitation of stannic oxide which inhibits the evaporation are encountered during the evaporation process. It is also an energy intensive operation.

Since suitable technology for the treatment of rinse-water from fluoborate plating baths is lacking, this investigation was undertaken. Two separate processes, ion flotation and electrodrolysis, were investigated as a possible close-loop treatment of the dilute and concentrated fluoborate containing wastestreams from the electroplating industry.

Ion Flotation

Flotation processes for use in separation of solid particles from liquids is an old, well-established process in waste removal (4,5) as well as in the process industries (6). For waste removal by flotation, the mechanism is to add a surface active agent to the wastewater and mix it well. This allows the surfactant to adhere to the particles in the water. Foaming through the introduction of air brings the surfactant-solids combination to the surface even though they are more dense than water. When an air bubble contacts the surfactant-particle combination, the weight of the particle is balanced by the buoyancy of the affixed air

bubbles, and the particle floats.

Ion flotation is a relatively recent process. The field has been explored by Sebba (7) in South Africa and Grieves (8) in the United States. The concept of ion flotation is different from particle flotation in that a complex is formed between the surfactant and the dissolved ion. In particulate flotation, the surfactant adheres to the particle, but in waste streams such as from metal finishing operations, there are no particles. The surfactant, therefore, must chemically react with the ion which is to be removed.

Most of the work done in the ion flotation field has been concerned with removing metal cations from solution with anionic surfactants. However, Grieves (9) has investigated the use of ion flotation for the removal of the anionic chromate ion, but there has been no research into the removal of the fluoborate ion using this process. Thus, the use of specific ion flotation for the treatment of fluoborate plating bath rinse-waters containing dilute concentration of fluoborate was investigated.

The part of the investigation dealing with dilute fluoborate rinse-waters was concerned with 1) determining the type and structure of the surfactant that favors the binding of the fluoborate ion with the surfactant, 2) understanding the mechanism of binding and those parameters such as pH, ratio of the amount of surfactant to fluoborate ion, and contact time which can influence the binding of the fluoborate ion to the surfactant, 3) identifying those process parameters such as air feed rate, air bubble size, air diffuser location, inlet feed direction and mixing time which can influence the optimum removal of fluoborate ion, and 4) evaluating this technology for the removal

of fluoborate ion from the rinse-waters resulting from nickel stripping, solder plating, tin plating and copper plating operations.

Also, the means to recover the surfactant and fluoborate ion for reuse in the treatment process and plating baths, respectively, was examined. Ultrafiltration was evaluated as an alternate to flotation for rapid separation of the fluoborate-surfactant complex from the rinse-waters.

Electrodialysis

Electrodialysis is a membrane process which can be used for the separation, removal or concentration of ionized species in aqueous solutions. The above is accomplished by using an electromotive force to selectively transport ions through an ion-exchange membrane. These ion-exchange membranes are permeable to either cations or anions, but not to both. The membranes are thin sheets of ion-exchange material reinforced by a synthetic fabric backing. The resin matrix is usually copolymerized styrene divinylbenzene, the exchange capacity being imparted by sulfonic acid groups for cation exchange membranes and quaternary ammonium groups for anion exchange membranes.

A simple electrodialysis system consists of an anode and a cathode, separated by an anion permeable membrane near the anode and a cation permeable membrane near the cathode. Thus a cathode chamber, an anode chamber, and a center chamber are formed. When the electric charge is applied, anions pass from the center chamber to the anode chamber while cations pass from the center chamber to the cathode chamber. Therefore, the concentration of salt in the center chamber is decreased. The application of a simple electrodialysis cell in the separation of a potassium sulfate solution is shown in Figure 1.

In practical electrodialysis installations (10), there are ten to

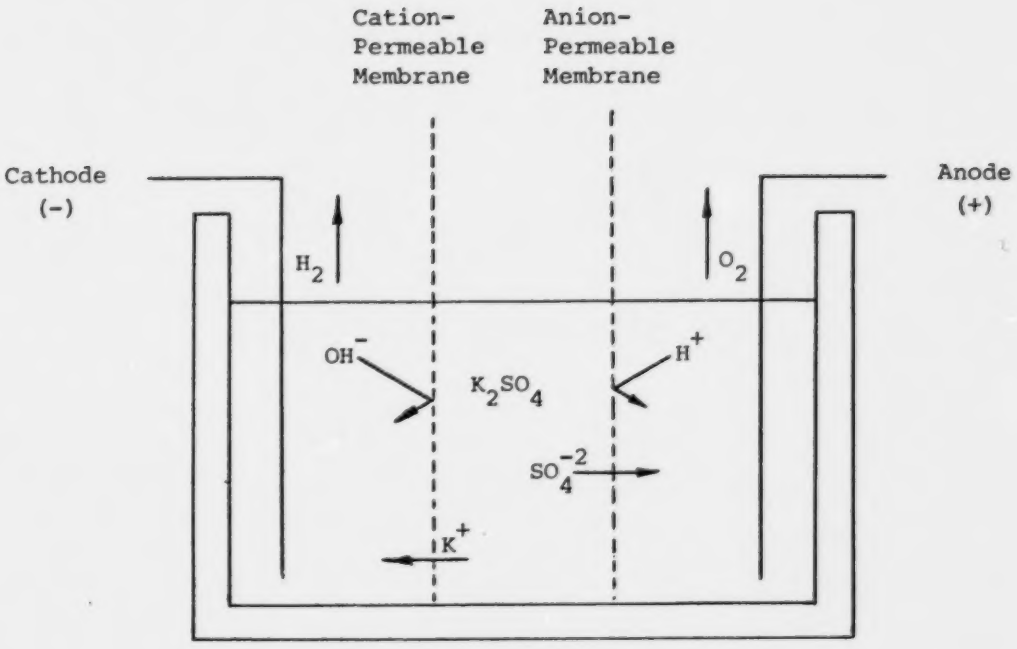

FIGURE 1. A SCHEMATIC OF A SIMPLE ELECTRODIALYSIS CELL

hundreds of compartments between one pair of electrodes. These units are referred to as electrodialysis stacks. These stacks include specially designed spacers to separate a cationic and anionic impermeable membrane and allow flow between adjacent membranes. The feed solution is distributed and the concentrate collected by two internal hydraulic channels; one for feed and one for concentrate. A cell pair includes the following components:

. Cation Selective Membrane

. Feed Spacer

. Anion Selective Membrane

. Concentrate Spacer

Passing a direct current through the stack causes ions to migrate across the permeable membranes from the feed channel and collect in the concentrate channel.

The most frequently used application of electrodialysis is in the desalination of brakish water (11). Some recent investigations relating to the metal finishing industry include the recovery of nickel and copper from plating rinse waters and closed-loop control of cyanide rinse-waters (11, 12). However, none have examined the use of electrodialysis as a means of treating fluoborate plating rinse-waters.

The feasibility of using electrodialysis as a means of treating concentrated tin, solder and copper fluoborate plating bath rinse-waters for recovery of the metal and fluoborate ion as well as reuse of the feed as rinse-water was investigated.

This study also involved the development and testing of an inexpensive new anode which could be used in an electrodialysis unit and be resistant to the corrosive properties of fluoboric acid electrolyte. The development of

this anode allowed fluoboric acid to be used as an electrolyte to match the anions present in the fluoborate waste stream.

The use of the traditional anodes such as the platinized titanium anode was unable to meet the corrosive nature of the fluoboric acid electrolyte. The use of this anode in an electrodialysis unit would require the use of less corrosive electrolytes such as sulfuric acid which can result in the contamination of the product with undesirable anions.

II. CONCLUSIONS

The specific ion flotation process used either separately or in combination with electrodialysis appears to be feasible for the close-loop treatment of waste rinse-waters resulting from solder, tin, nickel and copper plating operations. The combined use of both processes provides for recovery of plating bath chemicals at concentrations that approach plating bath strength with a treated effluent suitable for reuse as rinse-water.

Specific Ion Flotation

1. Specific ion flotation using a commercially available alkylamine acetate surfactant is feasible for the treatment of dilute rinse waste streams from solder, tin, nickel and copper plating operations to provide a product that can be reused as rinse-water.
2. Fluoborate anion concentration in the solder, tin and nickel fluoborate rinse wastestreams can be reduced to a concentration of 7 mg/1. Fluoborate anion in the copper plating bath rinse waters can be reduced to a concentration of 15 mg/1.
3. The removal of fluoborate anion by the surfactant is dependent on replacement of the acetate group on the surfactant by the fluoborate anion. Removals are inhibited by anions such as chloride, which form stronger acids than fluoborate acid.
4. Fluoborate anion removals are enhanced by an increase in the molecular weight of the surfactant and by acidic conditions, which increase the ionization of acetate groups on the surfactant.

5. Excess surfactant is required to make up for the acetate groups that are lost to the replacement reaction because of micelle formation which occurs at surfactant concentrations of 12 mg/1.

6. The replacement of the acetate group on the surfactant by the fluoborate anion occurs within one minute. The rate limiting step in this process is the mixing time required to achieve a complete mix upon addition of surfactant to a fluoborate wastestream by the laboratory system used in this study.

7. The fluoborate-surfactant complex can be removed from solution by aeration. Air bubble size, air diffuser location and inlet feed direction with respect to bubble rise, does not influence the rate of removal of the fluoborate-surfactant complex.

8. Increases in the air feed rate decreases the concentration of the fluoborate-surfactant complex in the foam by removing more liquid with the foam.

9. Ultrafiltration with recycling of the retentate provides a four times greater rate of removal of the fluoborate-surfactant complex from the rinse-water than aeration.

10. Electrolysis is suitable for splitting the fluoborate-surfactant complex to recover the surfactant. The surfactant is concentrated at the cathode and can be dissolved from the cathode in the acetate form with concentrated acetic acid.

Electrodialysis

1. Electrodialysis appears to be feasible for the treatment of concentrated fluoborate-containing rinse waste waters. It provides a product that approaches plating bath chemical concentrations and an effluent that can be

further treated by the specific ion flotation process.

2. The use of a high density, low porosity graphite anode in an electrodialysis unit provides greater resistance to chemical corrosion and a greater current density for a given applied voltage than the more commonly used platinized titanium anode.

3. The graphite anode's resistance to chemical corrosion permitted the highly corrosive fluoboric acid to be used as an electrolyte to match the anion in the feed.

4. The rate of transfer of stannous ion and lead ion from the feed to the concentrate is significantly greater than the rate of transfer of stannic ion from the feed to the concentrate. This difference in the rate of transfer of the cations minimizes the build-up of undesirable stannic ion in the plating baths from reuse of the electrodialysis product.

III. RECOMMENDATIONS

The recovery of plating bath chemicals and the closed-loop treatment using electrodialysis with newly developed graphite anode and specific ion flotation of rinsewater containing fluoborate anions from solder, tin, copper and nickel plating operations has been shown to be feasible. There are a a number of advantages in using electrodialysis and specific ion flotation for the treatment of rinsewater containing fluoborate. Electrolysis treatment preferentially concentrates the desirable stannous ions in the product stream from a mixture of stannous and stannic cations usually present in the rinsewaters. The product contains cation and anion concentrations that approach plating bath strength. The development of the graphite anode which is resistant to the corrosive nature of fluoboric acid provides an anode which is approximately one-fortieth the cost of the commonly used platinized titanium anode and allows the fluoborate electrolyte to be used to match the fluoborate anions present in the rinsewaters. The use of an electrolyte in the electrodialysis unit containing anions that match the anions in the feed is preferred to avoid contamination of the product produced from electrodialysis treatment. In addition, the surfactant used in the specific ion flotation treatment of rinsewaters containing low concentrations of fluoborate can be recovered along with the fluoborate anion by electrolysis.

In view of the above, the commercial feasibility of using electrodialysis in combination with specific ion flotation to provide a closed-

loop treatment system should be established on a pilot scale. The engineering parameters and costs associated with the design, assembly and operation of both systems must be determined. Also, this pilot scale effort should identify the methodology that will allow rapid mixing of the fluoborate rinse-waters with the alkylamine acetate surfactant solutions at concentrations that do not favor micelle formation. In addition, the long term stability of electrodialysis membranes (longer than 60 hours) toward the fluoboric acid electrolyte should be evaluated since frequent replacement of these membranes can lead to unacceptable operating costs. The substitution of the graphite anode after a period of time should not significantly contribute to the operating costs of the electrodialysis unit since its replacement cost is approximately one-fortieth of that required to restore the commonly used platinized titanium anode.

IV. EXPERIMENTAL

Ion Flotation

Surfactants

A number of different type surfactants were evaluated in this investigation. A literature search revealed that there were a number of different type surfactants that may bind to the fluoborate anion. However, there was no information to indicate the type of structure that would allow the surfactant fluoborate complex to be removed from solution either by air flotation or ultrafiltration and that would readily allow the surfactant to be separated from the anion for reuse.

A number of cationic surfactants were selected that differed in size, degree of saturation and structure. The cationic surfactants were evaluated because of the attraction that could be expected in solution between a positively charged surfactant molecule and a negatively charged fluoborate ion. Several non-ionic and anionic surfactants were investigated to determine if it would be possible to bind both the metal and the fluoborate to the surfactants for removal from solution.

The cationic surfactants evaluated were Amine O, Amine C, Amine S, Amine T, Ammonyx 220, Ammonyx T, Armac C, Armac T, Armac 18D, Armac H, Armac 8D, Duomac T, Atlas G-3634A and Finazoline T. The Ciba-Geigy Amine O, Amine C, Amine S and Amine T surfactants are heterocyclic tertiary amines.

The Ammonyx 220 and Ammonyx T obtained from Onyx are an alkyl dimethyl benzyl ammonium chloride and a cetyl dimethyl benzyl ammonium chloride, respectively. The Armac C, Armac T, Armac 18D, Armac HT, and Doumac T surfactants which were obtained from Armak are an alkylamine acetate (12-15 carbon atoms), an alkylamine acetate (16-18 carbon atoms), a distilled octadecane amine acetate (18 carbon atoms), a hydrogenated alkylamine acetate (16-18 carbon atoms), and an alkylamine diacetate, respectively. The Atlas G-3634A surfactant obtained from ICI is a quaternary ammonium derivative. The Finetex surfactant, Finazoline T, is an aminoethylimidazolene.

The nonionic surfactants used in this study, AmmonyxCDO, Onyxol 336 and Neutronyx, were obtained from Onyx and are an alkyl amido propyl dimethyl amine oxide, a lauric acid and an alkylphenol polyglycol ether with ethylene oxide, respectively.

The anionic organic phosphate surfactants used in this study were Dextrol OC-60, Dextrol OC-80, Dextrol OC-90, Dextrol OC-105 and Dextrol OC-110 and were obtained from Dexter.

Equipment and Procedures

The specific ion flotation experiments were carried out in a modified recirculation bath system (see Figure 2) designed to simulate an actual treatment process. The recirculation was required because the length of time required for the removal of the surfactant by air flotation was much longer than could be accomodated in a single flow-through tank. The equipment consisted of an eight liter holding tank, a two liter reaction vessel, an eighty liter per hour recirculation pump, and a twelve liter foam collector. The air for flotation was introduced through a porous

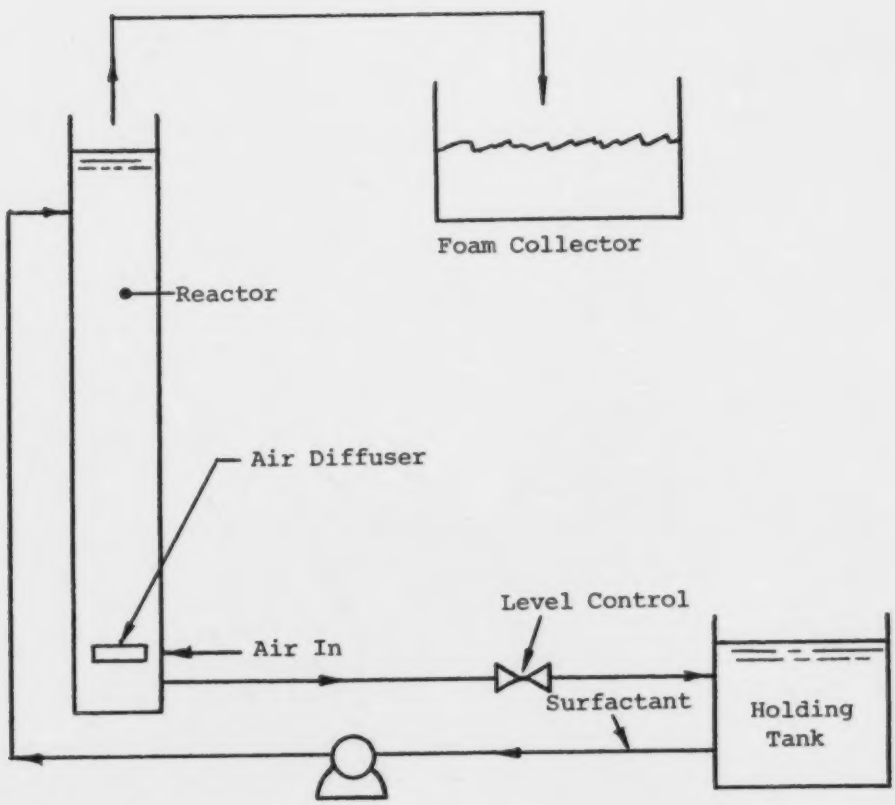

FIGURE 2. FLOTATION APPARATUS

stone diffuser, the air was controlled by a Brooks R-2-15 rotometer. The surfactant was introduced into the suction line of the pump using a twenty milliliter hypodermic syringe after fluoborate plating bath solutions were added and thoroughly mixed in the system. The syringe was used because even slow mixing in the pump caused foam to be generated in the holding tank during the makeup.

The system was cleaned by washing all tanks and tubing, and thoroughly rinsing them with deionized water after each experiment. The system was then charged with eight liters of deionized water. The desired quantity of sodium fluoborate or plating bath solutions was added to the deionized water and the solution recirculated for 36 minutes to assure thorough mixing. A series of tests in which the resulting dilute rinse-waters solutions were circulated through the system for different lengths of time up to 24 hours indicated that the test solutions were completely mixed within 36 minutes. The desired amount of surfactant, which had been dissolved in 200 ml of deionized water, was injected into the system at a rate of 8 ml per minute. The system was again recirculated for another 36 minutes to insure complete mixing of surfactant solution with the fluoborate solutions. Air was applied, and the solutions were recirculated continuously until there was no further generation of foam at the liquid surface in the reactor. The foam was then removed as formed.

Fluoborate Analysis

Analysis of the solution for the fluoborate ion was carried out using the series 92 and series 93 Orion fluoborate specific ion probes. The 93 series, which was determined to be the more sensitive probe, was used to analyze the solutions that contained no surfactants. The surfactant was observed to have an adverse effect on the probe's membrane. Therefore, the series 92 probe was used to measure the fluoborate concentration in the presence of the surfactant because its membranes could be replaced. It was determined that the membrane in the 92 series probe had to be replaced after the measurement of 10 solutions containing fluoborate ion and surfactant.

Micelle Formation

The critical micelle concentration was determined by conductivity measurement. A sharp decrease in the plot of conductance versus the square root of the surfactant concentration indicated the concentrations at which micelles begin to form.

Ultrafiltration

a. Simple Cell

The equipment used for initial evaluation of ultrafiltration for removal of the fluoborate surfactant complex from solutions was the Millipore Corporation's 47 mm stirred cell, catalogue number XX 42 047 10. The membranes were Millipore's Pellicon membranes, PSAC type.

The two membranes evaluated were the 1,000 and 10,000 nominal molecular weight limit (nmwl) membranes. The nmwl is a rough guide to the size above which most molecules are efficiently retained by that membrane.

The simple, stirred cell, which is depicted in Figure 3, is a cylindrical plastic unit designed to hold membrane discs for the ultrafiltration of small

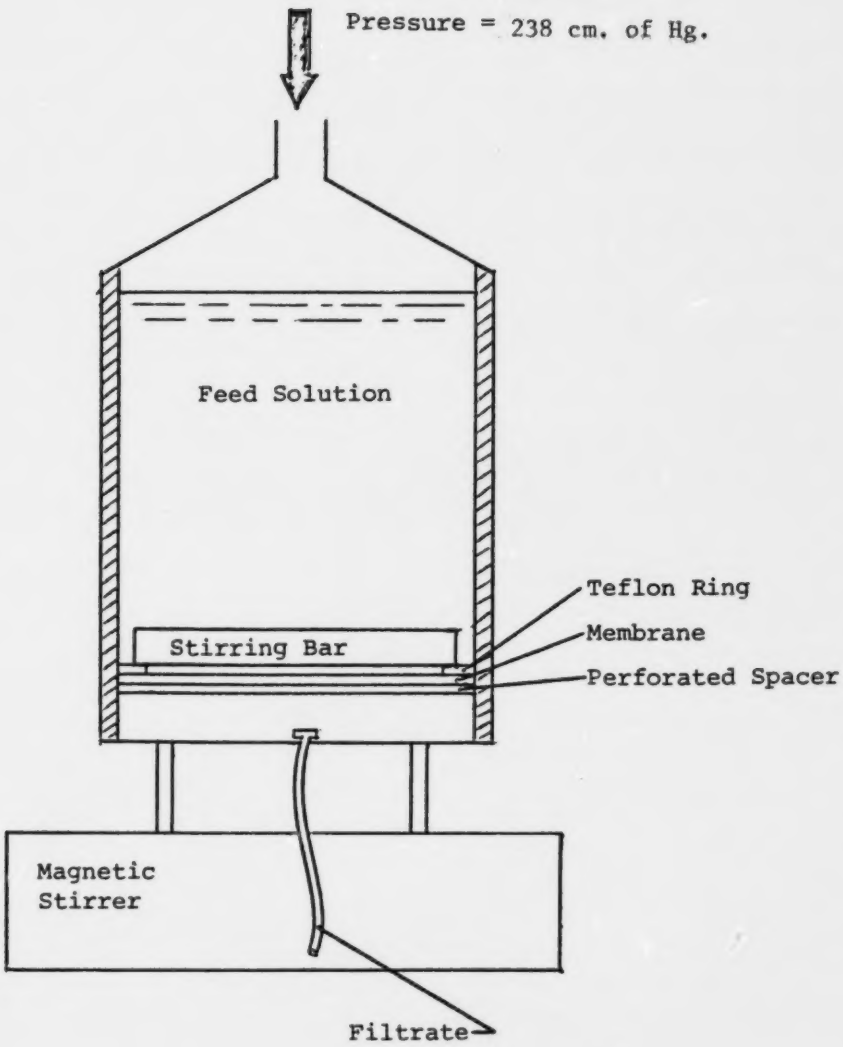

FIGURE 3. SCHEMATIC OF A SIMPLE ULTRAFILTRATION CELL

fluid volumes. The cell barrell is polycarbonate with silicone O-rings for seals at the base and cap. The capacity of the cell is 80 ml, the cell takes a 47 mm membrane disc which has a filtration area of 10.5 cm^2.

In the evaluation of the two different membranes, the set-up that is shown in Figure 3 was used. Seventy-five milliliters of solution was placed in the cell. The pressure applied to the feed solution was maintained at 238 cm. of Hg. The cell was mounted on a magnetic stirrer and stirred by means of a magnetic stirring bar inside the cell. This minimizes polarization occurring at the membrane. The filtrate was collected in test tubes from the plastic tube which was inserted in the base of the cell.

Initial experiments were run using a solution of 1500 mg/l of alkylamine acetate surfactant and 100 mg/l of fluoborate anion. During the evaluation of the 10,000 and 1,000 nmwl membrane a dye test was used to indicate the presence of alkylamine acetate surfactant in the filtrate. The dye test provided qualitative evidence of the presence or absence of alkylamine acetate in the filtrate solution by visual inspection.

Bromophenol blue, which was the dye that was used, gave a rough quantitative indication of the surfactant in solution. When the surfactant was present, a blue color was formed in the solution. When no surfactant was present the solution remained clear and colorless. The deepness of the blue increased as the concentration of surfactant increased. Therefore, the dye test was a good preliminary indication of the passage of the surfactant fluoborate complex through the ultrafiltration membrane.

The surfactant concentration in the ultrafiltration filtrate solution was analyzed using a Dorhmann Envirotech DC-52D Carbon Analyzer. The presence of fluoborate was observed to have no effect on this analysis.

b. High Volume Cassette

Further evaluation of ultrafiltration for the removal of the fluoborate-surfactant complex from solutions was carried out using the 100 nomimal molecular weight limit membrane in a Millipore High Volume Cassette System. The cassette system is 25 cm wide x 23 cm. deep x 30 cm. high. Membranes for this system have a filtration area of 465 cm^2.

The system was run utilizing a variable speed tubing pump to transport pressurized solution to the cassette's feed port. Pressure at the feed port was regulated by the pump speed. A needle valve was placed at the retentate port in order to maintain pressure over the entire membrane area. Using this system, two types of experiments were run: they were single pass flow and recirculating flow as depicted in Figures 4 and 5, respectively. During both experiments the same feed solution containing 1500 mg/1 of alkylamine acetate surfactant and 100 mg/1 of fluoborate was used.

Operating pressures were maintained at 155 cm of Hg at the feed port and 109 cm of Hg at the retentate port, during the single pass flow experiment. Due to the viscosity of the feed solution, only 5.7 ml of filtrate was collected per liter of feed. In order to remove more fluid from the sample than can be accomplished in one pass, the recirculating flow system was investigated.

During the recirculating flow experiment the retentate was run back into the sample vessel. The sample vessel was mounted on a magnetic stirrer and the solution was stirred to maintain a homogeneous feed. The pressures

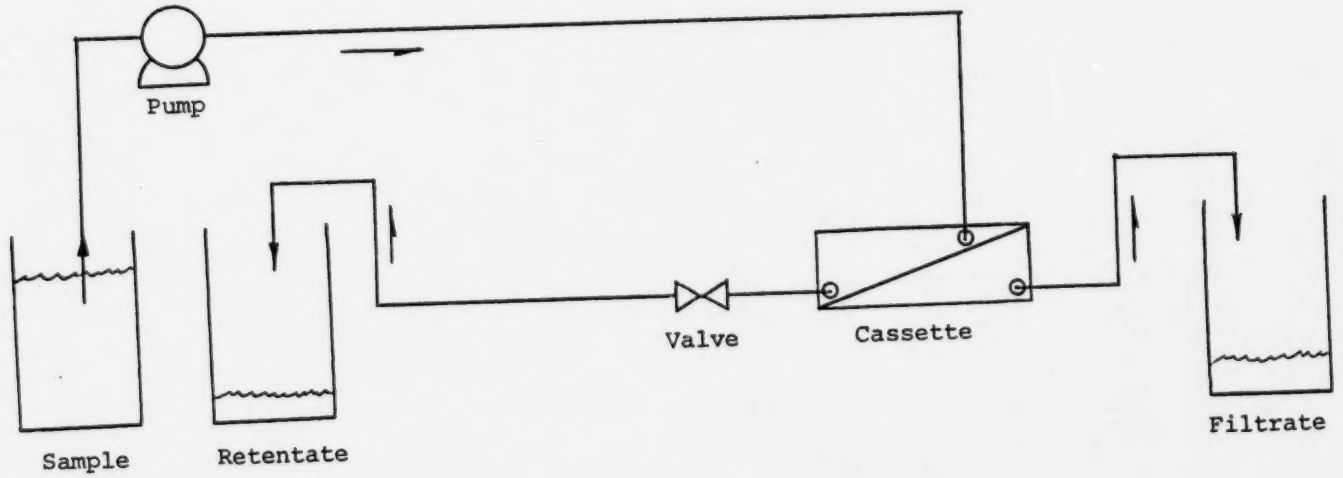

FIGURE 4. SINGLE PASS FLOW SYSTEM

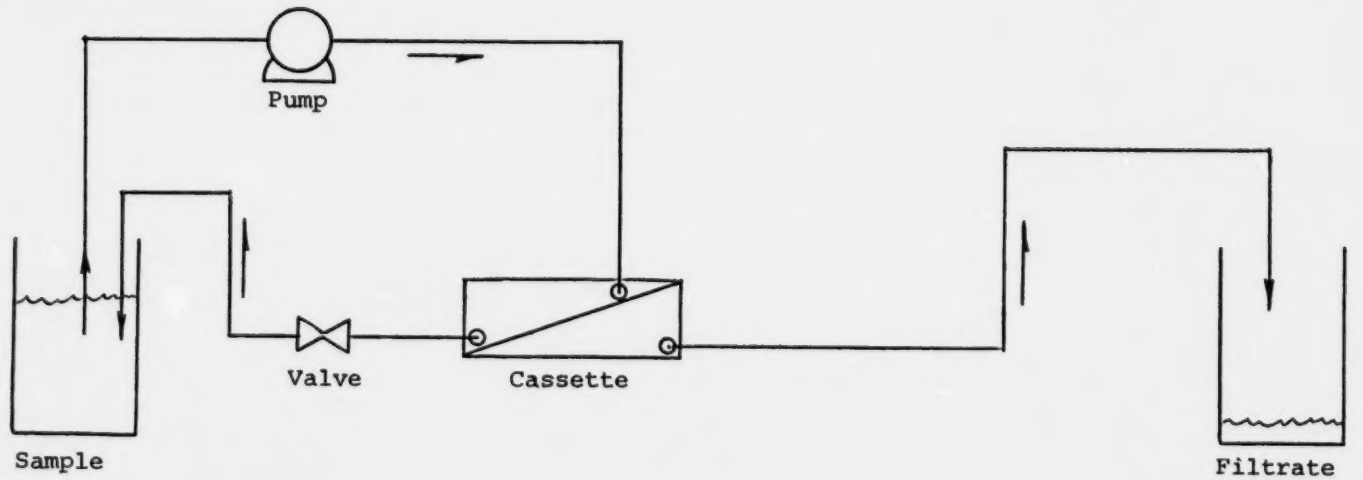

FIGURE 5. RECIRCULATING FLOW SYSTEM

were maintained at 155 cm. of Hg at the feed port and 114 cm. of Hg at the retentate port.

The filtrates from both the single pass flow and the recirculating flow experiments were analyzed for TOC to determine the surfactant-fluoborate complex removal.

Breaking the Fluoborate-Surfactant Complex

a. Addition of Excess Acetic Acid

In an attempt to reverse the equilibrium of the surfactant-fluoborate complex and break the complex, the addition of excess acetic acid was examined. A one liter solution of 100 mg/1 of fluoborate and 1500 mg/1 of alkylamine acetate surfactant was used. Concentrated acetic acid was pipeted into this solution at an initial volume of 0.5 ml. The solution was stirred utilizing a magnetic stirrer. The concentrated acetic acid was added in increments of 0.5 ml. After each addition of acid, the concentration of fluoborate anion was monitored using the Orion 92 series electrode system.

b. Electrolysis

Electrolysis was also investigated as a means for separating the surfactant-fluoborate complex. A simple electrolysis cell was set up as shown in Figure 6. The components were a pyrex beaker, a spiraled platinum anode, a copper cathode, and a direct current (D.C.) power supply.

The D.C. power supply was kept constant at 45 volts (1% ripple). This provided a current density at the cathode of approximately .004 Amps/cm^2.

A surfactant-fluoborate solution of 1500 mg/1 of alkylamine surfactant and 100 mg/1 of fluoborate anion was added to the system and then the power supply was turned on. Using the 92 series fluoborate specific ion electrode,

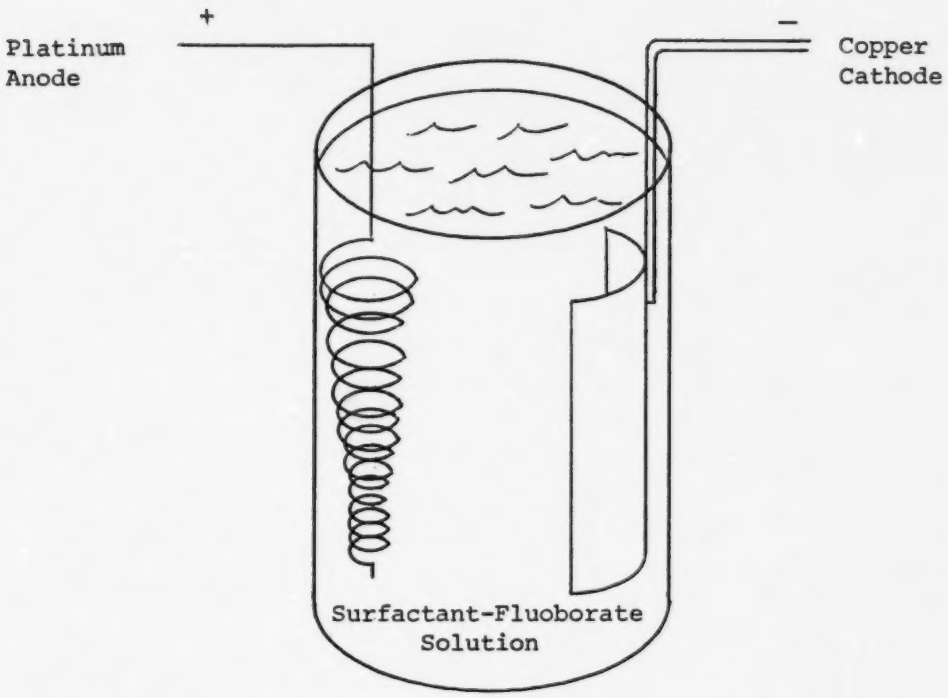

FIGURE 6. SCHEMATIC OF ELECTROLYSIS SET-UP

the fluoborate concentration was determined periodically. These concentrations were then plotted versus time to determine the rate of disassociation of the complex.

Using the above system, disassociation of the following four solutions were examined:

1. Solution A: surfactant (1500 mg/1) + sodium fluoborate (100mg/1); stirred for 90 minutes.
2. Solution B: Same constituents as Solution A; stirred for 8 hours.
3. Solution C: surfactant (1500 mg/1) + lead and tin fluoborate, fluoborate anion = 100 mg/1; stirred overnight.
4. Solution D: surfactant (1500 mg/1) + lead and tin fluoborate, fluoborate anion = 100 mg/1 + brighteners; stirred overnight.

2. Electrodialysis

Electrodialysis was investigated here as a means of concentrating fluoborate plating rinse-waters for recycle back to the plating bath. All plating bath rinse-waters were generated by diluting plating bath solutions with deionized water to desired metal cation and fluoborate anion concentrations. A Micro Pore (Hanover, Mass.) electrodialysis stack was used to carry out the electrodialysis experiments. The stack consisted of thirteen cell pairs and was arranged as illustrated in Figure 7. Each cell pair consisted of a Neosepta strongly acidic cation permeable (C66-5T) and strongly basic anion permeable (AFN) membranes (Tokuyama Soda Co Ltd., Japan).

The size of the membranes and electrodes was 55.9 cm x 30.5 cm. Approximately 63 percent of the area of the membranes was used for ion transfer.

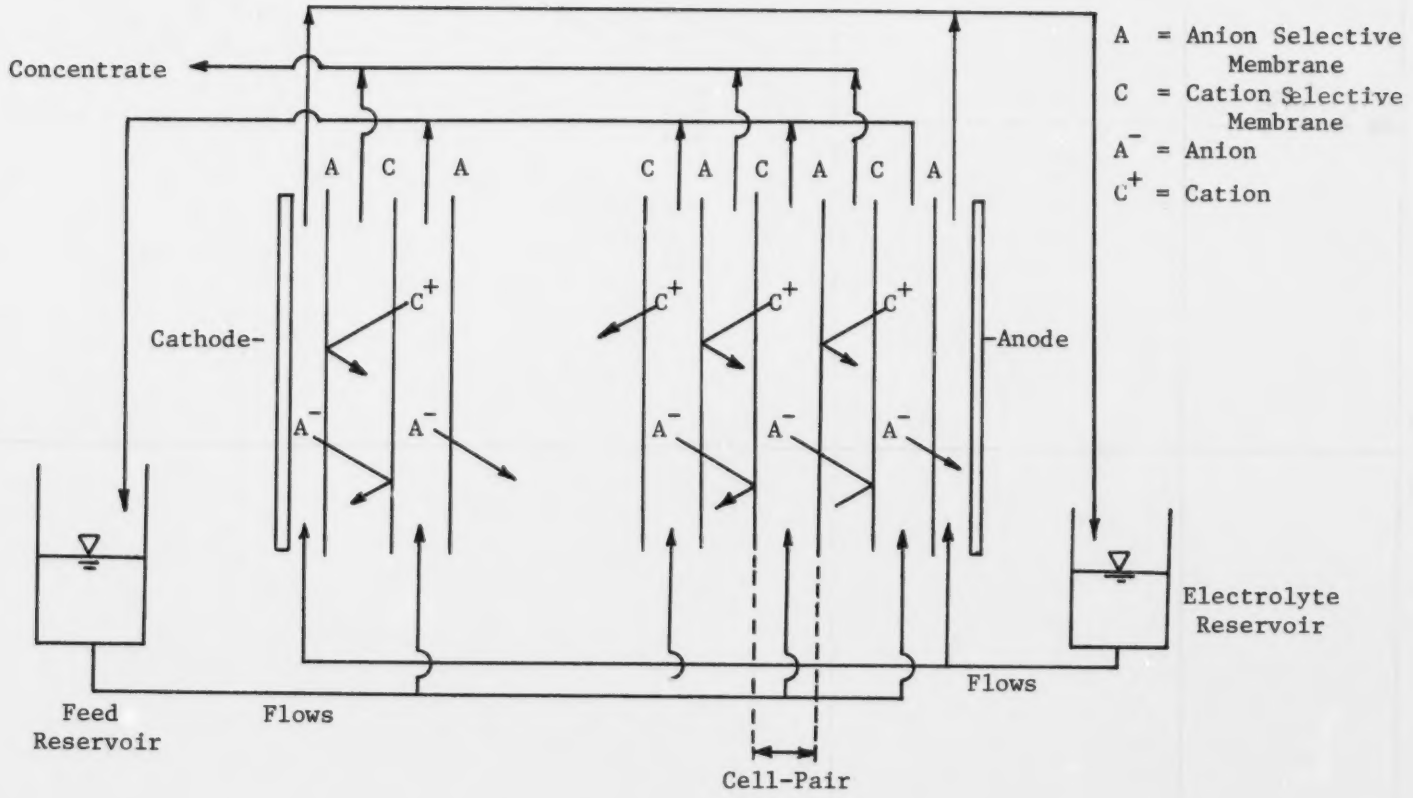

FIGURE 7. SCHEMATIC OF AN ELECTRODIALYSIS STACK

The spacers and membranes delineated an S-shaped flow pattern which incorporated the advantages of the more common sheet flow and tortuous path designs (see Figure 8). Alternate cells were connected to internal feed or product manifolds. An additional anion permeable membrane was used at the cathodes to prevent migration of the cations into the electrolyte and being reduced at the cathode. The ends of the stack were terminated with the two electrodes. The cathode was stainless steel 316 while the anode which was originally platinized titanium metal but had to be replaced because of corrosion problem. A hydraulically isolated electrode rinse solution consisting of a mixture of hydrofluoboric acid and sodium fluoborate was recirculated from an electrolyte reservoir.

Other related supplies included pumps for both the feed and electrolyte solution, reservoirs for 114 liters of feed and 38 liters of electrolyte collecting vessels for the concentrated products, and an exhaust over the electrolyte reservoir to remove electrolyte gases, a rectifier and necessary piping and valving. The complete installation is shown in Figure 9.

Initially, the electrolyte was recirculated through the cathode and anode cells at a rate of 133 1/hr., while the feed solution was recirculated through the feed cells at a rate of 456 1/hr. The D.C. power supply was then turned on and the current was brought up to 10 amperes by slowly increasing the voltage across the electrodes. The flows were regulated by gate valves to maintain a pressure of 52 cm. of Hg at both the electrolyte and feed inlets. Also, the temperature of the solution at the feed outlet was monitored in order to prevent possible membrane damage due to the overheating of the stack. At the end of each experiment, the flows were run for 2-3 minutes after the current was shut off. Also, between experiments the

FIGURE 8. SPACER ON GRAPHITE ANODE TO DEFINE S-SHAPED FLOW PATTERN

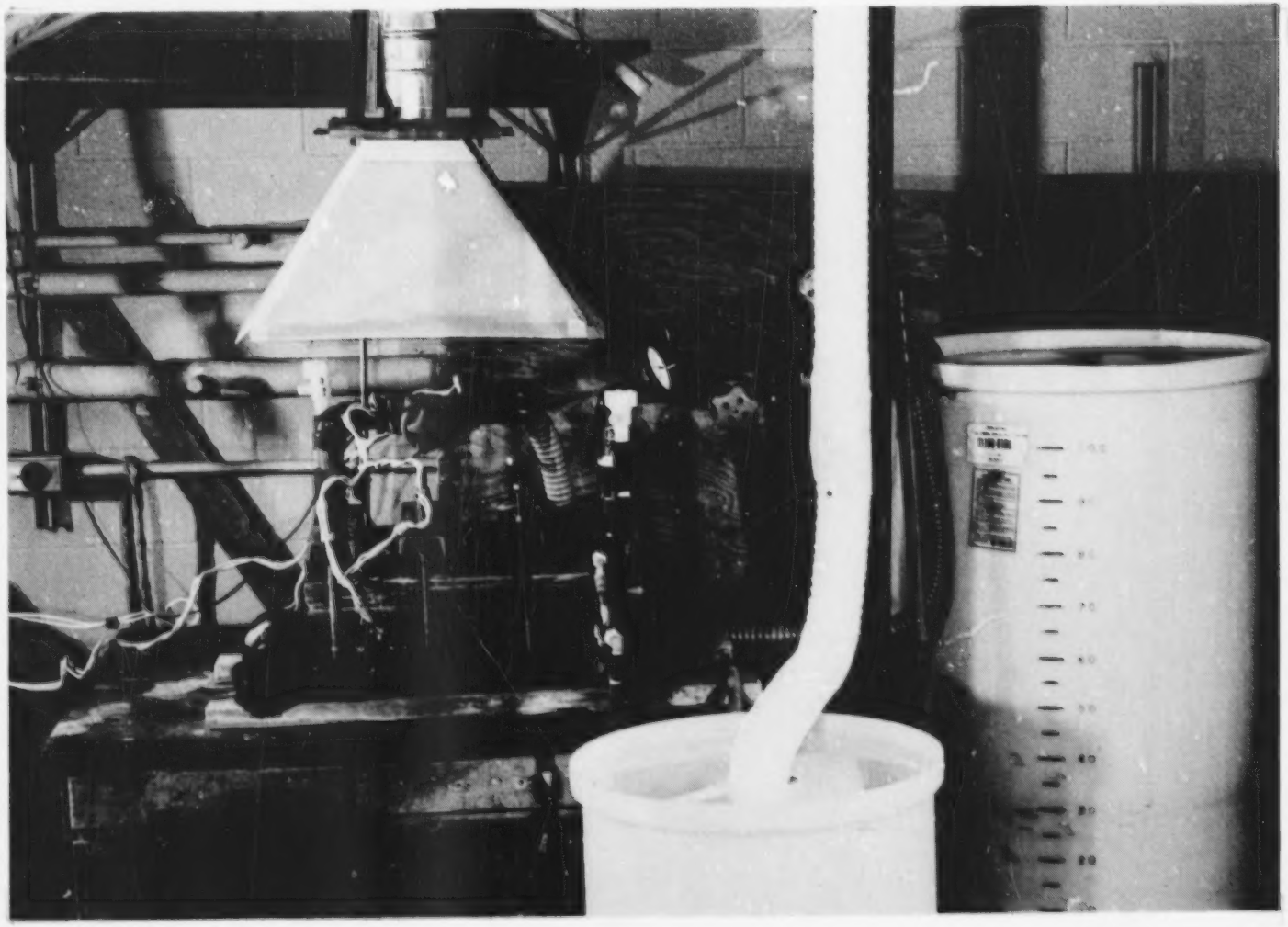

FIGURE 9. ELECTRODIALYSIS UNIT FEED RESERVOIR (tank on right)

AND ELECTROLYTE RESERVOIR (lower middle right)

stack was flushed with distilled water until no metal or fluoborate could be detected.

Feed, product and electrolyte samples were collected initially, at regular intervals during each run and at the completion of each run and analyzed for metal concentrations, fluoborate concentrations and pH. The pH was monitored to indicate whether there was a significant transfer of hydrogen ions from the feed to the product. The electrolyte was analyzed to detect metal ion breakthrough from the concentrate to the electrolyte at the cathode.

The concentration of total tin, copper and lead were analyzed after serial dilution with fluoboric acid solutions using a Varian Techtron Atomic Absorption Spectrometer (Model 1200). The serial dilutions were carried out to reduce the metal ions to levels that could be measured. Serial dilution of the samples with fluoboric acid solution at the same pH as the samples being analyzed was found to prevent precipitation of metal prior to analysis.

Stannous ion concentrations were determined according to Method 155 (14) by titration by 0.1 N and 0.01 N iodine solution to a blue iodine-starch complex end point. The fluoborate ion concentration was calculated using the Orion Model 93 series specific ion electrode.

V. RESULTS AND DISCUSSION

1. Ion Flotation

This part of the investigation was concerned with identifying the type of surfactant which would bind to the fluoborate ion. A number of cationic, anionic and non-ionic surfactants were initially evaluated using sodium fluoborate solutions. The cationic surfactants were primary, secondary and tertiary amines attached to various organic radicals. The non-ionic surfactants were the oxide of an aromatic amine, an aliphatic acid and acyclic ether. The anionic surfactants were of the organic phosphate type.

Significant fluoborate removal was observed with only two of the cationic surfactants, Duomac T and Armac C. Approximately 55 percent removal of the fluoborate was achieved with Armac C, the better of the two surfactants, during the initial surfactant screening. All of the other surfactants tested showed no significant removal of the fluoborate ion. The Duomac T and Armac C differ from the other surfactants examined in that both surfactants contain acetate groups. Apparently, the presence of the acetate group is required for the removal of the fluoborate by specific ion flotation.

Fluoborate ion removal could be increased from 55 to 82 percent by increasing the mole ratio of Armac C to fluoborate from 1.0 used in the initial screening to 3.0. A series of tests were performed on solutions containing different initial concentrations of sodium fluoborate and varying the specific mole ratios of Armac C to fluoborate ion to determine

the concentrations to which Armac C could reduce the fluoborate ion. The results indicate that at initial fluoborate concentrations of 100 mg/1 and below, the Armac C can reduce the fluoborate concentration to approximately 18 mg/1, using a surfactant to fluoborate mole ratio of 3:1 (see Figure 10). When the initial fluoborate concentration is raised to 150 gm/1, the Armac C reduced the fluoborate concentration to only 48 mg/1 using the same mole ratio of 3:1. These results appear to be due to the fact that not all of the surfactant required to provide a mole ratio of 3:1 to treat a fluoborate concentration of 150 mg/1 can be dissolved. An extremely turbid solution resulted. Thus, even though a 3:1 mole ratio of surfactant to fluoborate ion was prepared not all of the surfactant was available to react with fluoborate ion.

Factors Influencing the Removal of Fluoborate by the Surfactant

The results of the initial screening of the surfactants suggested that the acetate group on the surfactant molecule is involved in the removal of fluoborate ion. In order to test this further, factors which influence the removal of the acetate ion from the surfactant were examined. Sodium acetate was added to the Armac C surfactant so as to reduce the ionization of the acetate group. A 100 mg/1 of Armac C acetate solution when added to the fluoborate solution to provide a 3:1 mole ratio of surfactant to fluoborate resulted in only 63 percent removal of fluoborate ion. When no sodium acetate was added, an 82 percent removal of fluoborate was obtained. These results indicate that the binding of the fluoborate requires the removal of the acetate group from the surfactant through ionization of the surfactant to form a cation and an acetate ion.

If the above is the case, an increase in acidic conditions should also

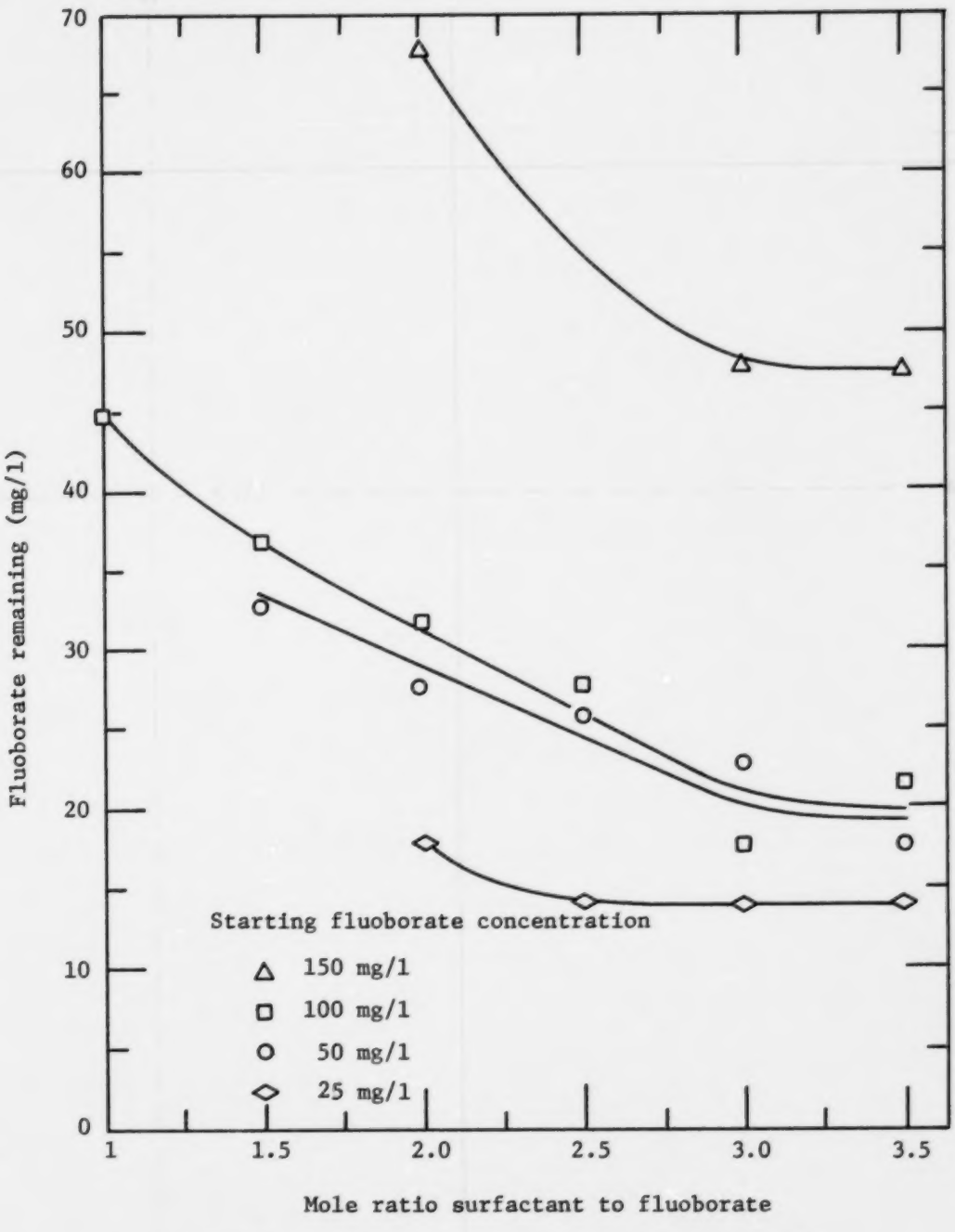

Figure 10. TREATMENT OF DILUTE SODIUM FLUOBORATE SOLUTION WITH ARMAC C

favor the removal of fluoborate by an acetate surfactant since acidic conditions would favor the formation of the surfactant cation through removal of the acetate ion from solution in the form of acetic acid. A reduction in the final pH of the surfactant-fluoborate solution was found to favor the removal of the fluoborate from solution by the Armac C. The use of fluoboric acid instead of sodium fluoborate in the mole ratio of 3:1 surfactant to fluoborate decreased the final pH from 6.2 down to 5.0. The removal of fluoborate was increased from about 87 percent up to 92 percent (see Table 1).

The influence of other anions which form stronger acids than fluoboric acid on the removal of the fluoborate by the surfactant was examined. Hydrochloric acid was added to separate solutions containing the 3:1 mole ratio of surfactant to fluoborate ion in amounts sufficient to provide final solutions that contained 50 mg/1 and 100 mg/1 of hydrochloric acid. Fluoborate ion removals of only 70 percent and 58 percent were obtained in the solutions containing the 50 mg/1 and 100 mg/1 of hydrochloric acid, respectively. Thus, the presence of anions which form stronger acids than fluoboric acid apparently inhibit the removal of the fluoborate by the surfactant.

The above results indicate that the fluoborate ion reacts with the surfactant by replacing the acetate group on the surfactant since it forms a stronger acid than acetic acid. However, maximum removal of the fluoborate in these experiments is achieved with a surfactant to fluoborate mole ratio of 3:1. The use of the 3:1 mole ratio indicates that 3 acetate groups are involved in the removal of one fluoborate ion since each Armac C surfactant molecule contains only one acetate group. The need for excess surfactant suggested that all acetate groups are unavailable for replacement by the fluoborate ion.

TABLE 1. Effects of pH on Removal of Fluoborate Ion

mg/l Fluoborate as		pH			
HBF_4	$NaBF_4$	Initial	Surfactant	Final	% Removal
100	0	3.7	6.0	5.0	92
75	25	3.8	6.0	5.6	92
50	50	4.1	6.0	5.8	89
40	60	5.4	6.0	6.2	86
30	70	7.1	6.2	6.2	83
25	75	6.7	6.1	6.1	87
0	100	7.4	6.0	6.3	87

The results of three stepwise additions, maintaining a mole ratio of 1:1 of surfactant to fluoborate remaining in the resulting solution after removal of the surfactant-fluoborate complex reduced the amount of surfactant required to remove a specific number of molecules of fluoborate.

Only 2.06 millimoles (554 mg) of total surfactant reduces 1.15 millimoles of fluoborate (100 mg) in one liter to 0.21 millimoles (18 mg) by stepwise addition of decreasing amounts of surfactant (see Table 2). The fluoborate which reacted with the surfactant was removed by aeration after each addition of surfactant. In contrast, a single addition of 3.45 millimoles (810 mg) of surfactant was required to reduce the 1.15 millimoles of fluoborate in one liter of solution to the 18 mg.

Micelles were observed to form at surfactant concentrations above 12 mg/1. This could limit the number of surfactant acetate groups that are available for replacement by the fluoborate. Since the fraction of the total surfactant molecules in solution that exists as micelles generally decrease as the surfactant solution becomes more dilute, the stepwise addition of decreasing amounts of surfactant to a given amount of fluoborate would increase the fraction of total acetate available for replacement by the fluoborate ion. Thus, it appears that stepwise addition of very dilute solutions of surfactants to minimize the micelle formation should require less surfactant to react with a specific amount of fluoborate.

In order to further understand the selective fluoborate ion removals exhibited by the surfactant containing the acetate group, surfactants similar to Armac C but differing in carbon chain length and degree of saturation were investigated.

The effect of surfactant molecular size on the removal of the fluoborate

TABLE 2. Fluoborate Removal Using Stepwise Addition of Armac C Surfactant to Sodium Fluoborate

Concentration of Armac-C		Concentration of Fluoborate		Fluoborate Concentration remaining after aeration
mg/l	millimoles	mg/l	millimoles	mg/l
310	1.15	100	1.15	52
160	0.60	56	0.60	27
84	0.31	27	0.31	18

ion in a solder plating bath rinse-water containing 100 mg/l of fluoborate ion was studied using Armac C (12-15 carbon atoms), Armac T (16-18 carbon atoms) and Armac 18D (18 carbon atoms). The results show that as the chain length of the surfactant is increased from the C_{12-15} to C_{18}, the percent fluoborate removed is increased from approximately 80 percent up to 97 percent when using the surfactant to fluoborate mole ratio of 3:1 (see Figure 11). The treatment of the solder bath rinse-water with the surfactant containing the 18 carbon atoms results in only 3 mg/l of the fluoborate ion remaining in the rinse-water. Reduction of the fluoboric ion concentrations in the solder rinse-water to below 3 mg/l using surfactants with chain lengths greater than 18 carbon atoms was not possible because of the marked decrease in solubility exhibited by the surfactants with larger molecular sizes than Armac 18C.

The degree of saturation of the surfactant does not appear to effect the removals of the fluoborate ion. The removals of fluoborate ion in solder bath rinse-water achieved with Armac HT whose percent saturation is 97 percent is comparable to that achieved with Armac T whose percent saturation is only 58 percent. This is observed for the range of surfactant to fluoborate ion mole ratios studied (see Figure 12).

The reaction of the fluoborate ion with the surfactant occurs within a relatively short period of time. The mixing of Armac C with fluoborate in mole ratio of 3:1 resulted in the reduction of fluoborate ion from 87 mg/l to 18 mg/l within 1 minute (see Figure 13). These results indicate that a contact time of one minute between the surfactant and fluoborate is required for the replacement of the surfactants' acetate group by the fluoborate ion prior to removal by aeration.

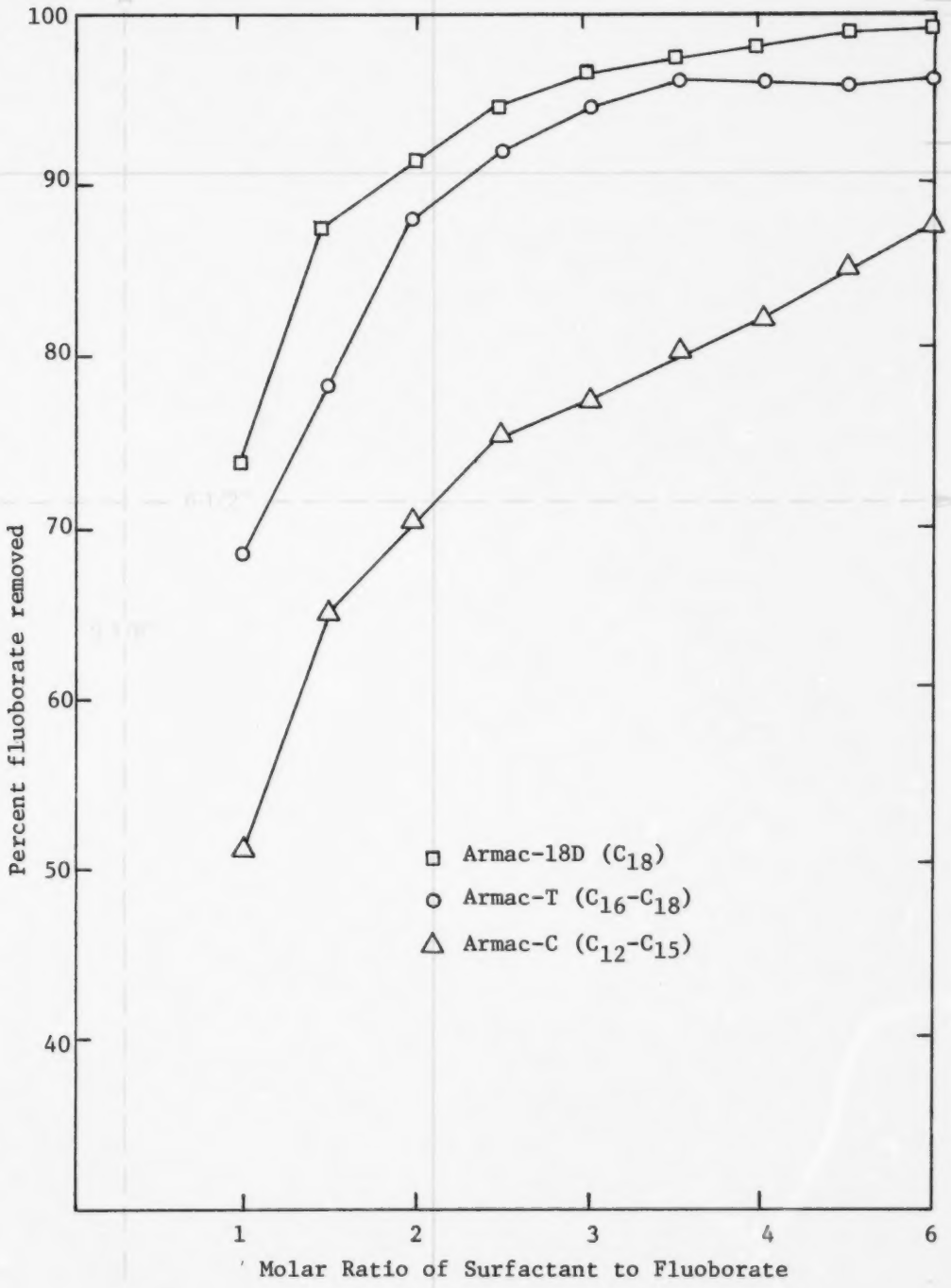

FIGURE 11. FLUOBORATE REMOVAL FROM SOLDER RINSE-WATER DEPENDENCE ON SURFACTANT MOLECULAR SIZE

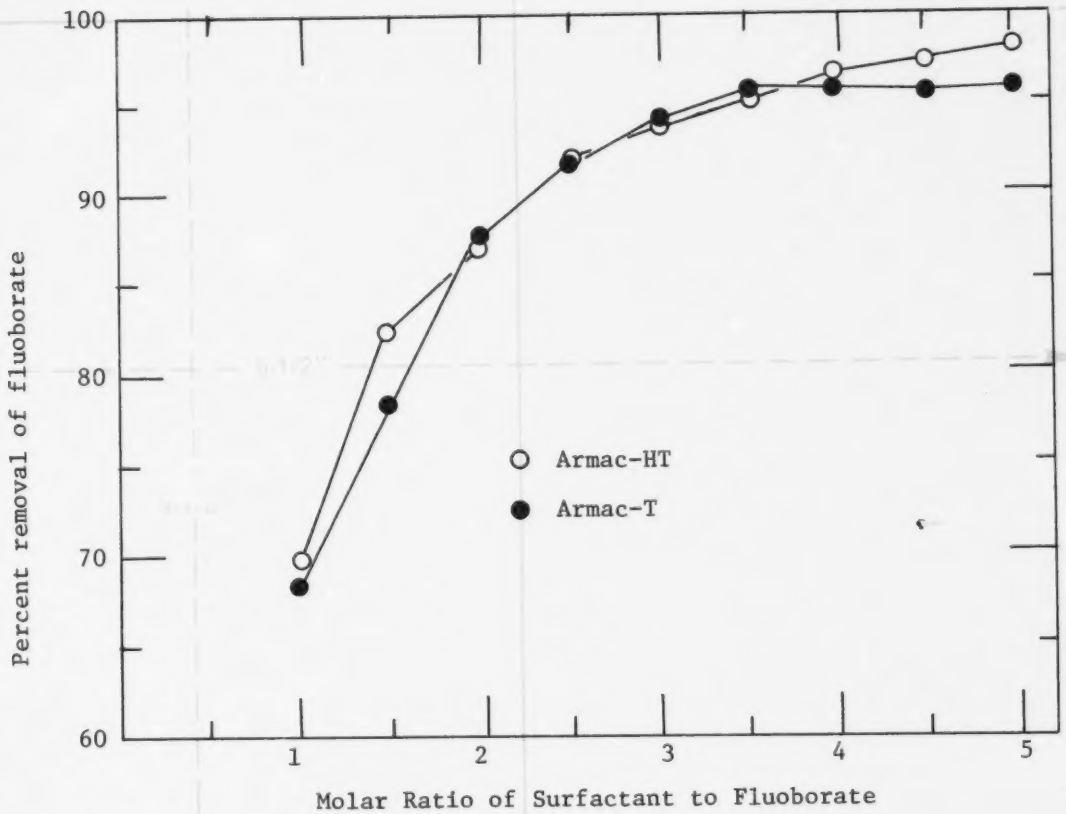

FIGURE 12. FLUOBORATE REMOVAL FROM SOLDER RINSE-WATER DEPENDENCE ON SURFACTANT DEGREE OF SATURATION

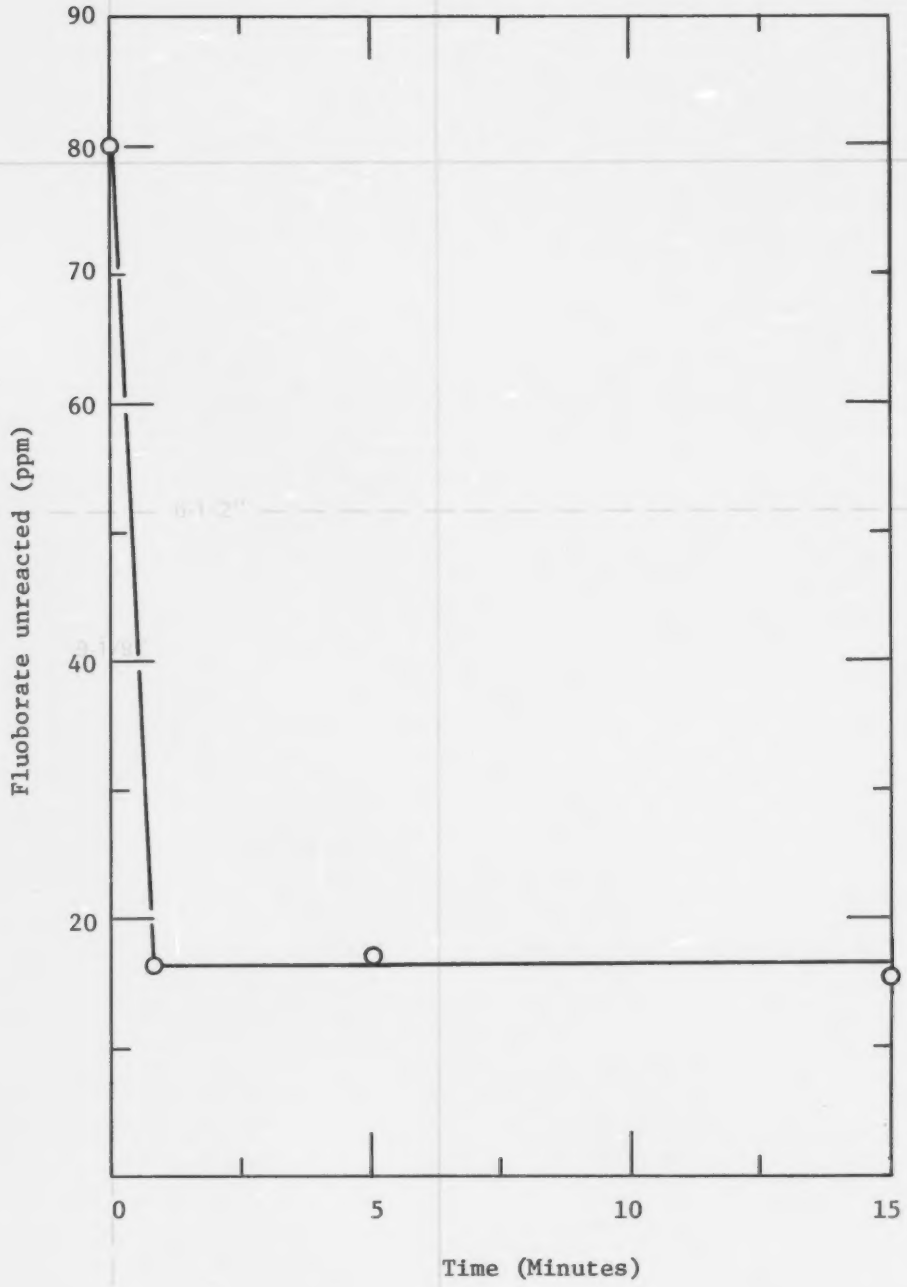

FIGURE 13. TIME OF REACTION OF FLUOBORATE WITH SURFACTANT

Process Parameters

Changes in air feed rate, air bubble size, air diffuser location, inlet feed direction, and mixing time on the removal of the surfactant-fluoborate complex from solution by aeration were investigated because these factors can influence the performance of bubble columns (15, 16).

Varying the air feed rate from 4 cc/sec. to 30 cc/sec. using a 3:1 mole ratio of Armac C to fluoborate did not improve the rate of removals of fluoborate and surfactant from solution. In both cases, time in excess of 20 hours was required to remove all of the surfactant. However, an increase in the air feed ratios does augment the amount of solution that is carried over in the foam. This results in a wetter foam and a reduction in the concentration of the surfactant-fluoborate complex in the foam. For example, two foaming operations were carried out at air feed rates of 15 cc/sec. and 30 cc/sec. were used. The lower air feed rate provided a resulting foam with a surfactant-fluoborate complex concentration of 4000 mg/1 whereas the higher air feed rate provided a foam with surfactant-fluoborate complex concentration of less than 1000 mg/1.

Neither changes in bubble size, air diffuser location nor inlet feed directions with respect to the rising air bubbles were observed to influence the removal of the surfactant-fluoborate molecule in the bubble column. Separate experiments using 3:1 mole ratio of Armac C to fluoborate ion in which 1) initial air bubble diameters of 0.003 and 0.007 were generated in the column, 2) positioning the air diffuser location at 10 cm. and 30 cm. below the surface of the liquid in the columns to increase the contact time between the bubble and the solution, and 3) introducing the feed into the column counter-current as well as perpendicular to the rising air

bubble did not improve the rate of removals of the surfactant-fluoborate complex. Times in excess of 20 hours were required to remove all of the surfactant for each of the above experiments. However, these results indicate that significant variation can occur in the bubble size, and contact time between the air bubble and the solution without influencing the rate of removal of the fluoborate-surfactant complex.

Removal of Fluoborate from Plating Rinse-Waters

A series of tests were performed on rinse-water containing 100 mg/1 of fluoborate ion by adding different amounts of Armac T to different rinse-waters that are representative of that obtained from solder plating, tin plating, nickel stripping, and copper plating operations. Armac T rather than Armac 18D which provided greater removals of fluoborate ion was used for these studies because it is far less expensive. It was felt that in practice the slightly better removals achieved earlier with Armac 18D did not warrant the additional expense.

The results indicate that Armac T can reduce the fluoborate concentration from 100 mg/1 to approximately 7 mg/1 in the solder, tin and nickel stripping rinse-water using a surfactant to mole ratio of 3:1. The fluoborate ion in the copper plating rinse-water is only reduced to approximately 15 mg/1 (see Figure 14). This is probably due to the fact that the pH of the copper plating rinse-waters is less acidic than the other plating bath rinse-water.

The above results are significant in that they indicate that the removal of fluoborate with surfactant is comparable with that which can be achieved with lime precipitation of fluoride in wastestreams. The widely used lime precipitation of fluoride in wastestreams results in a fluoride ion residual

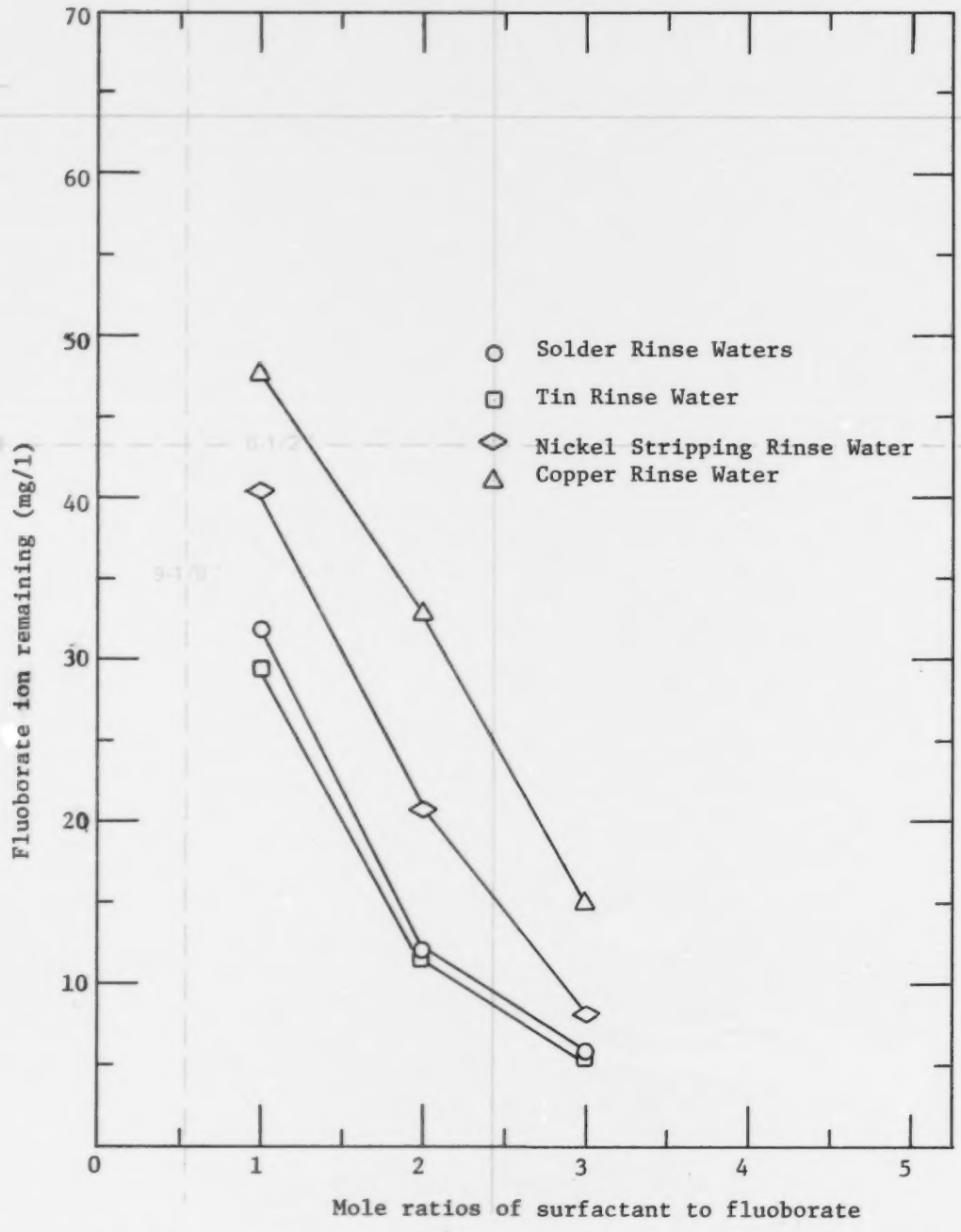

FIGURE 14. REMOVAL OF FLUOBORATE FROM PLATING BATH RINSE WATERS WITH ARMAC T

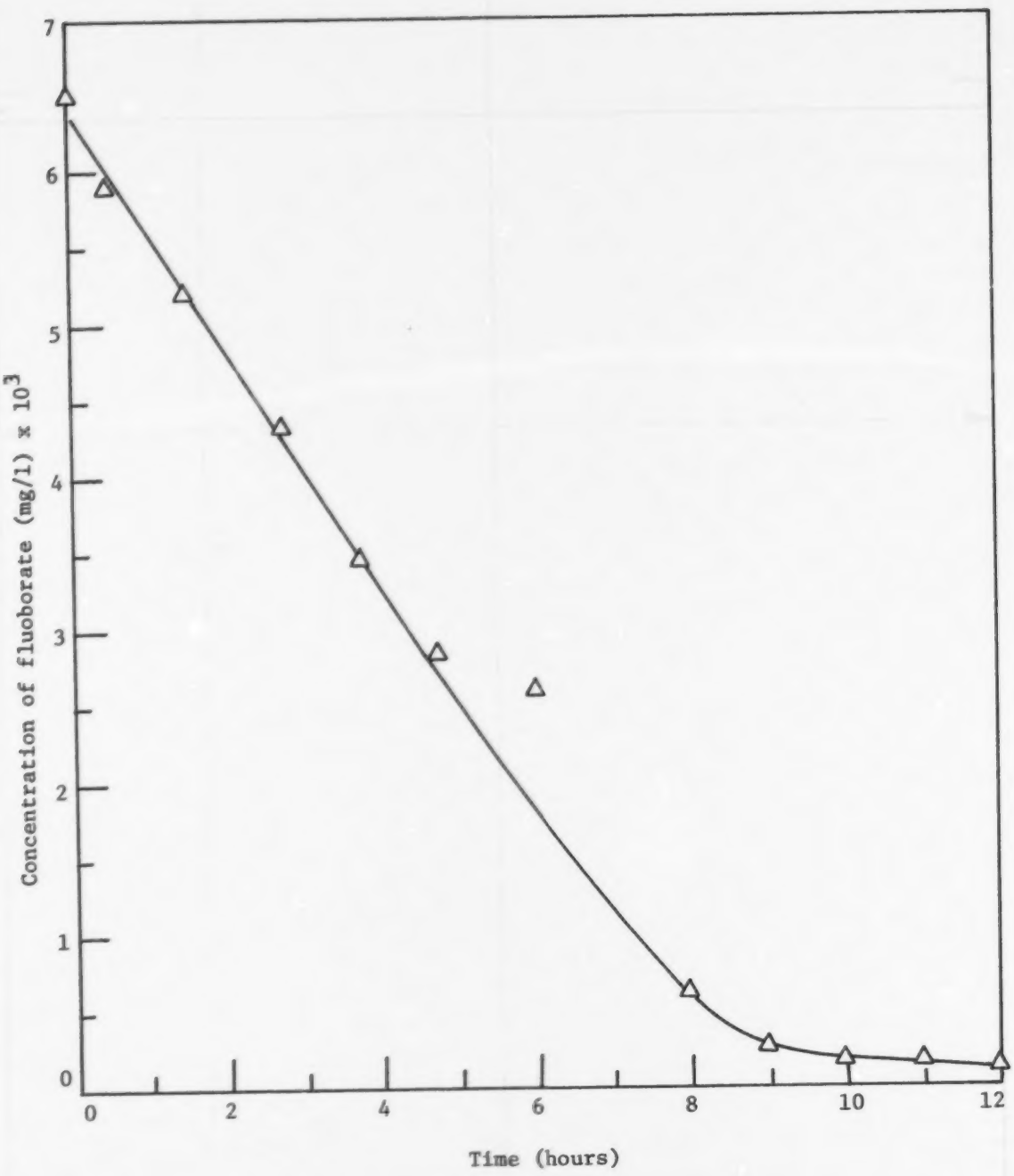

FIGURE 19. TREATMENT OF TIN FLUOBORATE RINSE-WATERS, FEED ANION CONCENTRATION

of about 8 mg/l in the wastestream (17). Thus, where fluoride concentrations of 8 mg/l in discharges are acceptable, the use of surfactant treatment of fluoborate should also be acceptable.

Recovery of Surfactant

Application of specific ion flotation as a close-loop process for treatment and recovery of plating bath rinse-waters containing fluoborate necessitates recovery and reuse of the surfactant. Thus, means to break the surfactant-fluoborate complex must be available.

Two approaches were evaluated for breaking the surfactant-fluoborate complex. These were 1) displacing the fluoborate by the addition of excess amounts of concentrated acetic acid and 2) separation of the surfactant from the fluoborate by electrolysis. It was found that the addition of concentrated acetic acid failed to reverse the equilibrium and displace the fluoborate from surfactant. Even with the addition of copious quantities of acetic acid, only a small amount of fluoborate was liberated from complex.

Electrolysis of the surfactant-fluoborate complex was then assessed. The electrolysis of the fluoborate-surfactant solution shows the liberation of approximately 90 percent of fluoborate ion originally removed by the surfactant (see Figure 15). In this electrolysis process the surfactant is plated out on the cathode as the complex is broken and causes the initial turbid solution to become clear. Concentrated acetic acid was found to remove the surfactant as the acetate. In the acetate form, the surfactant can be reused for the fluoborate removal in plating operation wastestreams.

Ultrafiltration

Foaming times in excess of 20 hours were required in the reactor to remove all the surfactants. Thus, ultrafiltration was examined as an

alternate more rapid process for removing the surfactant-fluoborate complex. Evaluation of the ultrafiltration membranes utilized a low through-put pressure cell. In the cell, experiments were run with 10,000 and 1,000 molecular weight cut-off membranes. Experiments with the 10,000 molecular weight cut-off membrane were unsuccessful. The solution passed right through the membrane.

The 1,000 molecular weight cut-off membrane was effective in filtering a solution of plating rinse-water containing fluoborate ions complexed with the Armac T surfactant. Removals of Approximately 79 percent were achieved (see Table 3) in the low through-put cell as determined by total organic carbon measurements.

Although the molecular weight of Armac T surfactant is approximately 330, it was determined from conductivity that the Armac T forms micelles at concentrations greater than 12 ppm. Therefore, at the concentration of surfactant that is required to complex the fluoborate, it will exhibit an apparent molecular weight much greater than 330.

Experiments utilizing the 1,000 molecular weight cut-off membrane by recycling the retentate in a Millipore Cassette ultrafiltration apparatus showed favorable results. Recycling the retentate back into the ultrafiltration cassette resulted in a removal of surfactant of 85 percent (see Table 4).

These ultrafiltration experiments produced the same results as air flotation. However, times in excess of 20 hours were required to achieve maximum removal of the surfactant-fluoborate complex from solution using air flotation. The recycled ultrafiltration experiments achieved this separation in approximately 5 hours. The ion flotation time cannot be

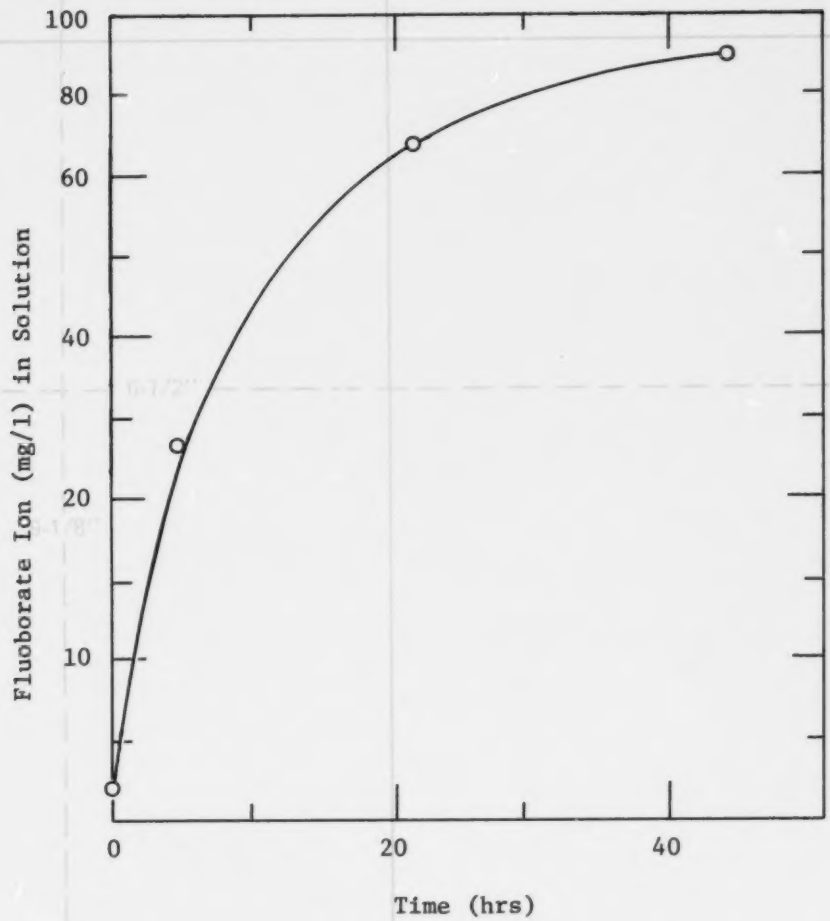

FIGURE 15. ELECTROLYSIS OF SURFACTANT FLUOBORATE CONCENTRATED SOLUTION FROM TREATMENT OF SOLDER BATH RINSE-WATER

TABLE 3. Removal of Surfactant with a Low Through-Put Ultrafiltration Experiment

Solution	Volume (ml)	TOC (mg)
Initial	75	80
1st filtrate collected	1.2	0.13
2nd filtrate collected	2.6	0.56
3rd filtrate collected	10.6	2.12
4th filtrate collected	43.0	10.06
5th filtrate collected	2.4	0.54
Total	59.8	13.5

$$\% \text{ Surfactant fluoborate retained by membrane} = \frac{\text{initial conc. - filtrate conc.}}{\text{initial conc.}} \times 100 = 79$$

TABLE 4. Results of Recycled Retentate Experiment, Millipore Cassette

Solution	Volume (ml)	TOC (mg)
Initial	1,000	1,073
1st filtrate collected	20	1.72
2nd filtrate collected	50	8.65
3rd filtrate collected	10	1.65
4th filtrate collected	50	9.25
Total	130	21.3
% surfactant fluoborate retained by membrane	$\frac{\text{initial conc. - filtrate conc.}}{\text{initial conc.}}$	x 100 = 85

reduced by industrial scale-up; however, the time required for ultrafiltration can be minimized by increasing the number of membranes used in the ultrafiltration unit.

Electrodialysis

Countercurrent or series rinsing of products from fluoborate plating operations can lead to fluoborate concentrations equal to or in excess of 1000 mg/l. For these highly concentrated wastewaters ion flotation treatment is not suitable. Thus, electrodialysis was investigated as a means to pretreat these concentrated rinse-waters to recover and reuse the plating reagents lost to rinse-waters and reduce the plating chemicals in the effluent to levels suitable for ion flotation treatment.

Application of electrodialysis for treatment of rinse-water containing high concentration of plating reagents required modification of an existing electrodialysis unit. Rapid deterioration of the commonly used platinized titanium anode was encountered when fluoboric acid is used as the electrolyte. Although this anode has been successfully used with nickel sulfate plating bath rinse-waters and a sulfuric acid electrolyte, it quickly turns black, cracks, and peels from the titanium metal backing when voltage is applied in the presence of fluoboric acid electrolyte (see Figure 16, Photograph of Corroded Platinum Anode). Apparently, the smaller fluoborate ion can penetrate the porous platinum coating and corrode the metal bond between the platinum and the titanium.

The matching of the anion in the electrolyte with that in the rinse-waters is preferred to using another anion such as sulfuric acid electrolyte which is non-corrosive to the platinized titanium anode. The sulfuric acid electrolyte would result in introduction of undesirable sulfate anion into

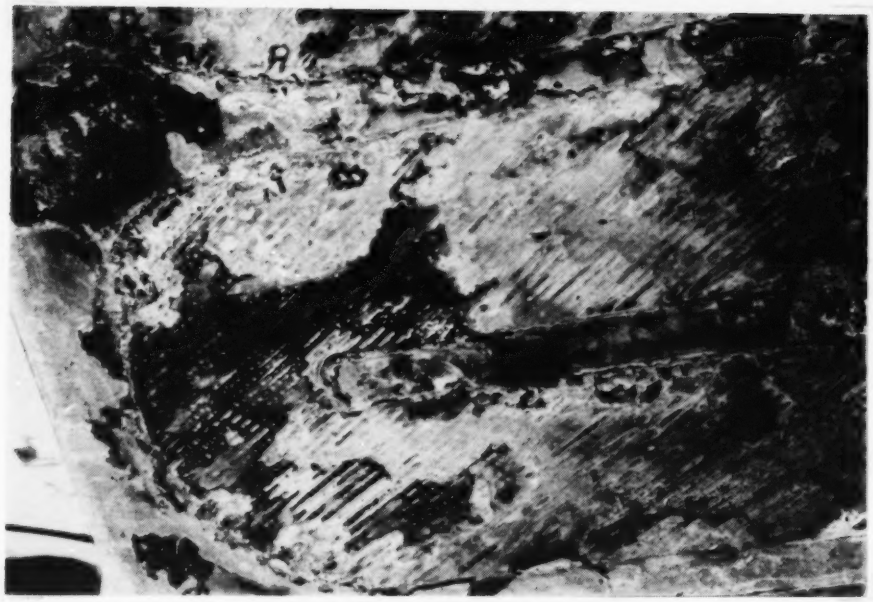

FIGURE 16. PHOTOGRAPH OF CORRODED PLATINIZED TITANIUM ANODE

the concentrate stream and ultimately the plating bath.

Evaluation of Different Types of Anodes

Several different approaches were considered to obtain an anode that would not corrode in presence of fluoboric acid electrolyte. These were 1) to increase the thickness of the platinum plated on the platinized titanium anode, 2) to plate a less porous metal such as gold on nickel backing and 3) examine the use of inexpensive conducting materials such as low porosity high density graphite to which voltage could be applied directly.

An increase in the thickness of the platinum plated on the titanium anode from 1.5 micrometers to 3.9 micrometers did not improve the anode's ability to withstand the corrosive properties of the fluoboric acid electrolyte. The platinum cracked and peeled away from the anode within an hour after voltage was applied to the anode in the presence of the fluoboric acid electrolyte.

Gold when plated on nickel and heated under controlled conditions can form a solid solution at the interface between the gold and nickel. This concept was utilized to achieve a bond between the gold and nickel backing at the interface. It was anticipated that the solid solution at the interface would resist the peeling and cracking that was encountered with the platinized titanium anode in the presence of the fluoboric acid electrolyte.

A series of experiments were carried out in which gold was plated on nickel strips and heated for 30 minutes and 45 minutes at temperatures of 1000°F, 1250°F and 1500°F, under a reducing atmosphere of hydrogen. Microprobe scan of the interface between the nickel and gold revealed that heating the anode at 1250°F for 45 minutes resulted in the nickel just

completely diffusing through the gold to the outer gold surface, whereas a heating time of 30 minutes resulted in the nickelforming a solid solution through 80 percent of the gold layer. This latter strip was selected to be evaluated for its resistance to corrosion by the fluoboric acid electrolyte because only the gold surface would be exposed to the fluoboric acid electrolyte.

Application of a voltage to this gold nickel anode strip to achieve a current density of .07 amps/cm^2 while immersed in the fluoboric acid electrolyte resulted in the gold layer peeling from the nickel backing (see Figure 17). Apparently, the solid solution between the gold and nickel at the interface does not resist the corrosive properties of fluoboric acid electrolyte.

Two graphite anode strips obtained from Union Carbide, Carbon Products Division, Chicago, Illinois, Grade AGXC and Stackpole, St. Mary, Pa. Grade LXB were evaluated to determine if they are resistant to the corrosive properties of fluoboric acid electrolyte under an applied voltage. Visual inspection revealed that neither graphite strips exhibited any deterioration when immersed in fluoboric acid electrolyte under applied voltage to provide a current density of .07 amps/cm^2. As a result, two anodes were fabricated for use in the electrodialysis unit and their performance evaluated under actual operational conditions.

The Union Carbide anode was observed to exhibit appreciable leakage of the fluoboric acid electrolyte from its sides. Encasement of this anode in a plastic coating did not prevent this leakage.

The use of the Stackpole high density low porosity graphite anode of the electrodialysis unit proved to be successful. There was no leakage of

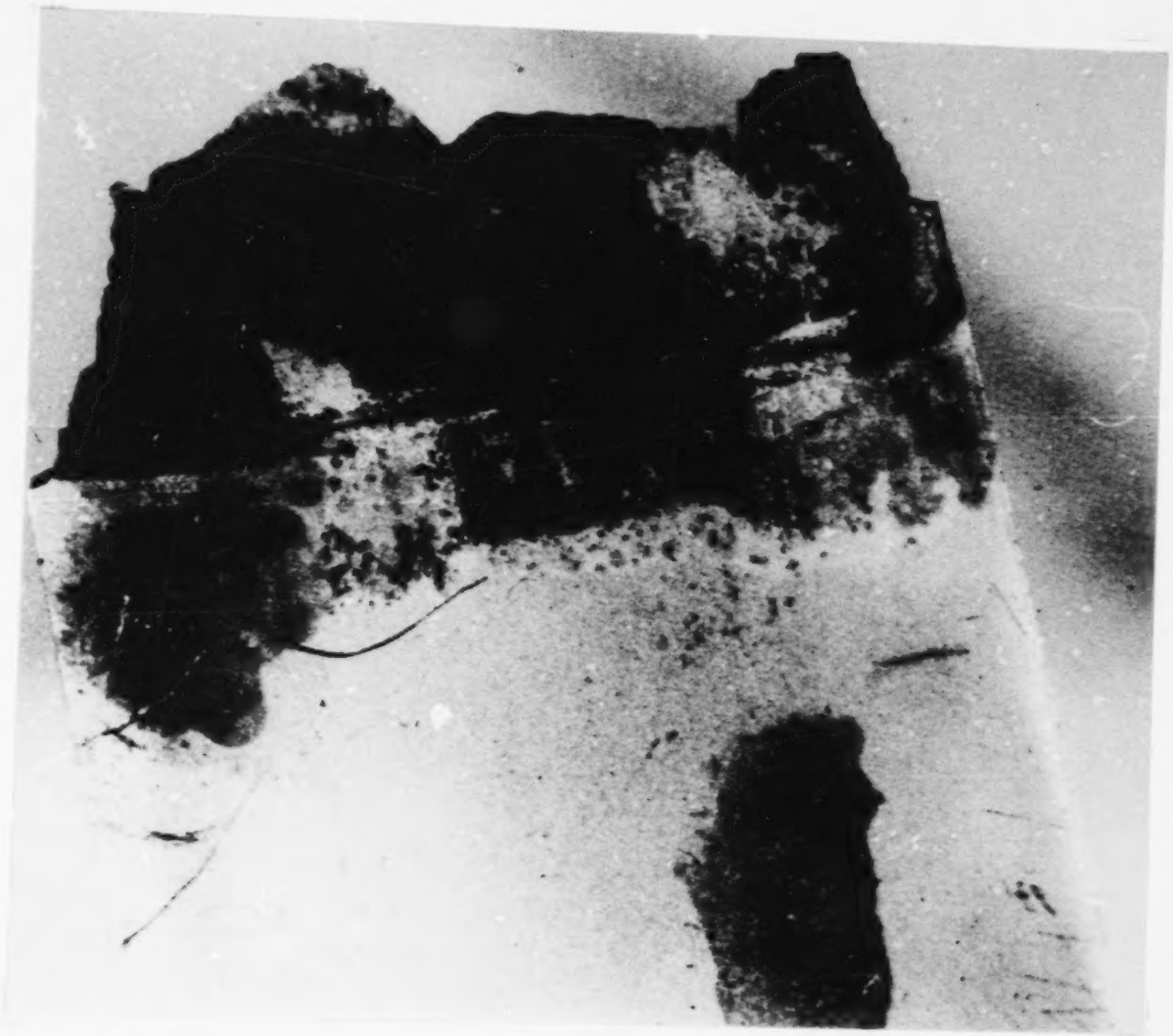

FIGURE 17. PHOTOGRAPH OF CORRODED NICKEL ANODE

fluoboric acid electrolyte from the anode and a greater current was achieved for a given applied voltage than that obtained with the widely used platinized titanium anode. The use of the graphite anode in the electrodialysis unit containing 13 ion pairs of membranes produce 10 amperes of current with an applied voltage of 10 volts. In contrast, the use of the platinized titanium anode in the electrodialysis unit containing the 13 ion pairs of membranes required 15 volts to produce the same 10 amperes of current.

Electrodialysis Result

In the treatment of concentrated rinse-waters prepared by diluting tin, solder and copper fluoborate plating bath solutions was carried out in the electrodialysis unit containing the Stackpole high density low porosity graphite anode and 13 ion pair membranes. The voltage across the anode and cathode was adjusted to maintain 10 amperes of current for all the experiments. The effectiveness of electrodialysis was evaluated for reducing the concentrations of metal and fluoborate ions in the rinse-water to levels which would allow the effluent to be treated using the ion flotation process, while providing a product with concentrations of metal and fluoborate ions that would approach that needed in the plating baths.

Treatment of Tin Fluoborate Rinse-Waters

A volume of 114 liters of tin fluoborate rinse-water containing 2400 mg/1 of stannous ion, 525 mg/1 stannic ion and 6500 mg/1 of fluoborate ion was treated by electrodialysis. After 12 hours of operation using 13 ion pair membranes at .012 amperes/cm^2 current density, the stannous ion concentration in the feed was below measurable levels. The stannic ion was reduced to 75 mg/1 and the fluoborate ion was reduced to concentrations below 150 mg/1 (see Figure 18). The stannous ion is reduced to concentration levels approaching

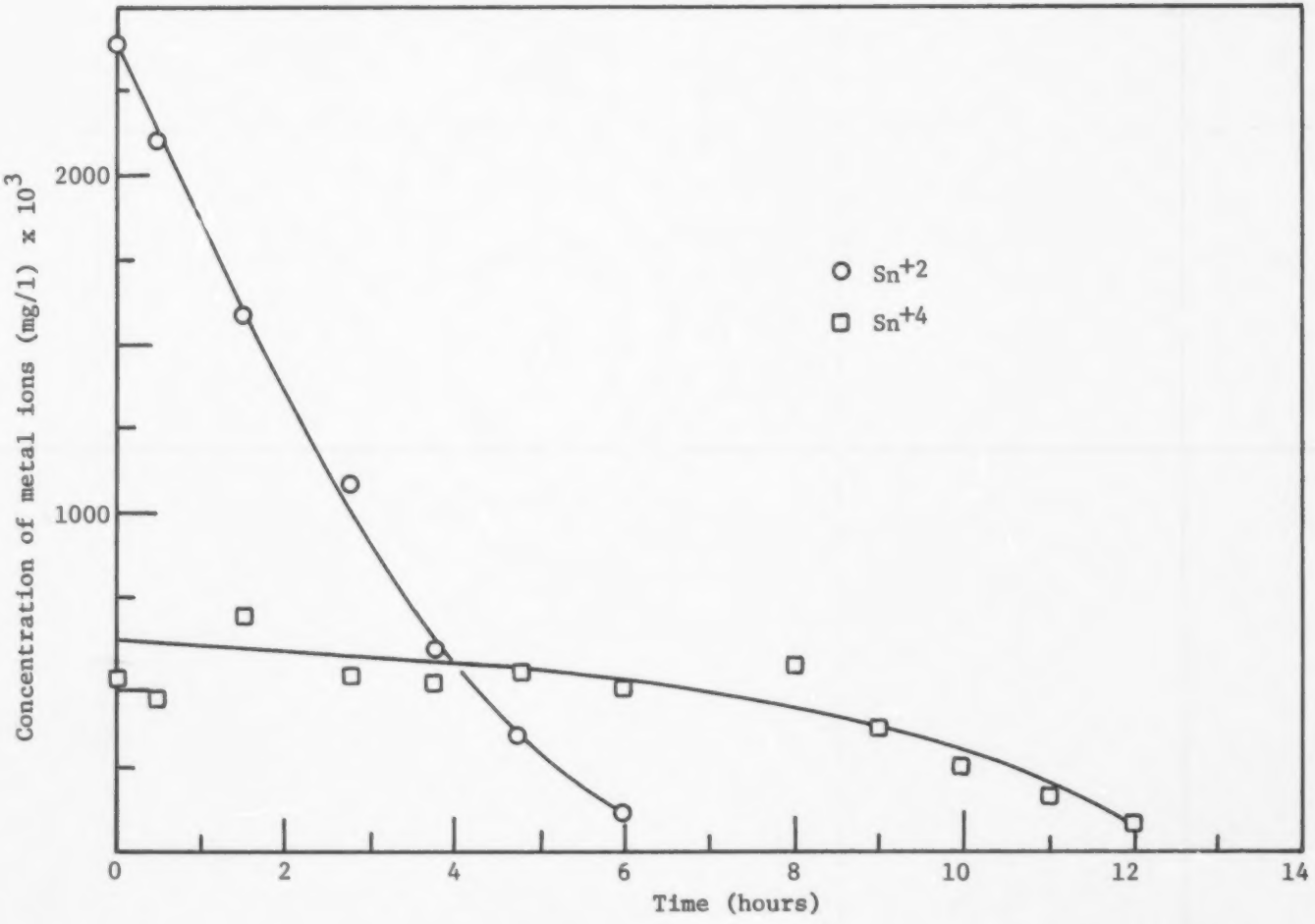

FIGURE 18. ELECTRODIALYSIS TREATMENT OF TIN FLUOBORATE RINSE-WATERS, FEED CATION CONCENTRATION

zero within 8 hours. The stannic ion on the other hand is removed at a much slower rate than the stannous ion from the feed over the initial 8 hours. The rate of removal of stannic ion increases after removal of the stannous ion.

The most rapid decrease in fluoborate concentration in the feed appears to occur within the initial 8 hours of operation. During this period the fluoborate ion concentration is reduced from 6500 mg/1 down to about 500 mg/1 (see Figure 19). This amounts to a removal of about 92 percent. The last four hours of operating the electrodialysis unit reduces the fluoborate concentration from 500 mg/1 down to below 150 mg/1.

The above results are of interest because they indicate that the plating chemicals in the feed can be reduced to levels acceptable for ion flotation treatment. Also, the stannous ion which is the desirable ion in plating baths is preferentially removed from the feed. Thus, the product from the electrodialysis unit should be enriched with stannous ion.

The analysis of the initial product from the electrodialysis unit shows a 30 fold increase in the stannous and fluoborate ions concentration. The stannous ion in the initial product collected is about 73,000 mg/1 after 2 hours of operation and decreases to 17,500 mg/1 (see Figure 20) as the concentration of stannous ion in the feed is further depleted. The fluoborate anion in the initial product is about 200,000 mg/1 and decrease to 100,000 mg/1 in six hours of operation (see Figure 21). This decrease is expected since the concentration of a specific ion in the product is reported (13) to be proportional to that in the feed. The stannic ion concentration in the initial product is about 7500 mg/1 and decreases to about 5000 mg/1 within six hours due to reduction in stannic ion in the feed from 565 mg/1

down to 500 mg/1.

The percent stannous ion in the product is observed to remain essentially well above 80 percent even though the stannous ion in the feed has been reduced from 83 percent down to 23 percent (see Table 5).

These results reflect the greater rate of removal of the stannous ion from the feed than the stannic ion.

The total amount of product generated in six hours from the treatment of 114 liters of feed was roughly 4.3 liters. This amounts to a volume ratio of product to feed of about 1:27. The concentration of tin and fluoborate in the product was 45 gm/1 of stannous ion, 6.7 gm/1 of stannic ion, and 140 gm/1 of fluoborate ion. The stannous and fluoborate ions in the product represent approximately one-half and one-third, respectively, of the concentration of stannous and fluoborate ions required for plating bath strength. The product collected in the initial six hours of operation represent a recovery of 95 percent of the stannous ions, 48 percent of the stannic ion and 70 percent of the fluoborate ion originally present.

Treatment of Solder Fluoborate Rinse-Waters

The treatment of solder fluoborate plating bath which contains stannous, stannic, lead and fluoboric ions in its rinse-waters was carried out under the same conditions employed for the treatment of the tin fluoborate plating bath rinse-waters. Greater than 97 percent reductions in the stannous ion and lead ions in the feed was achieved in eight hours. The time of operation was not extended beyond these 8 hours because it was shown earlier that the stannic ion and fluoborate ion concentration in the feed could be reduced to levels acceptable for treatment by ion flotation.

The stannous ion is again observed to be preferentially removed from the

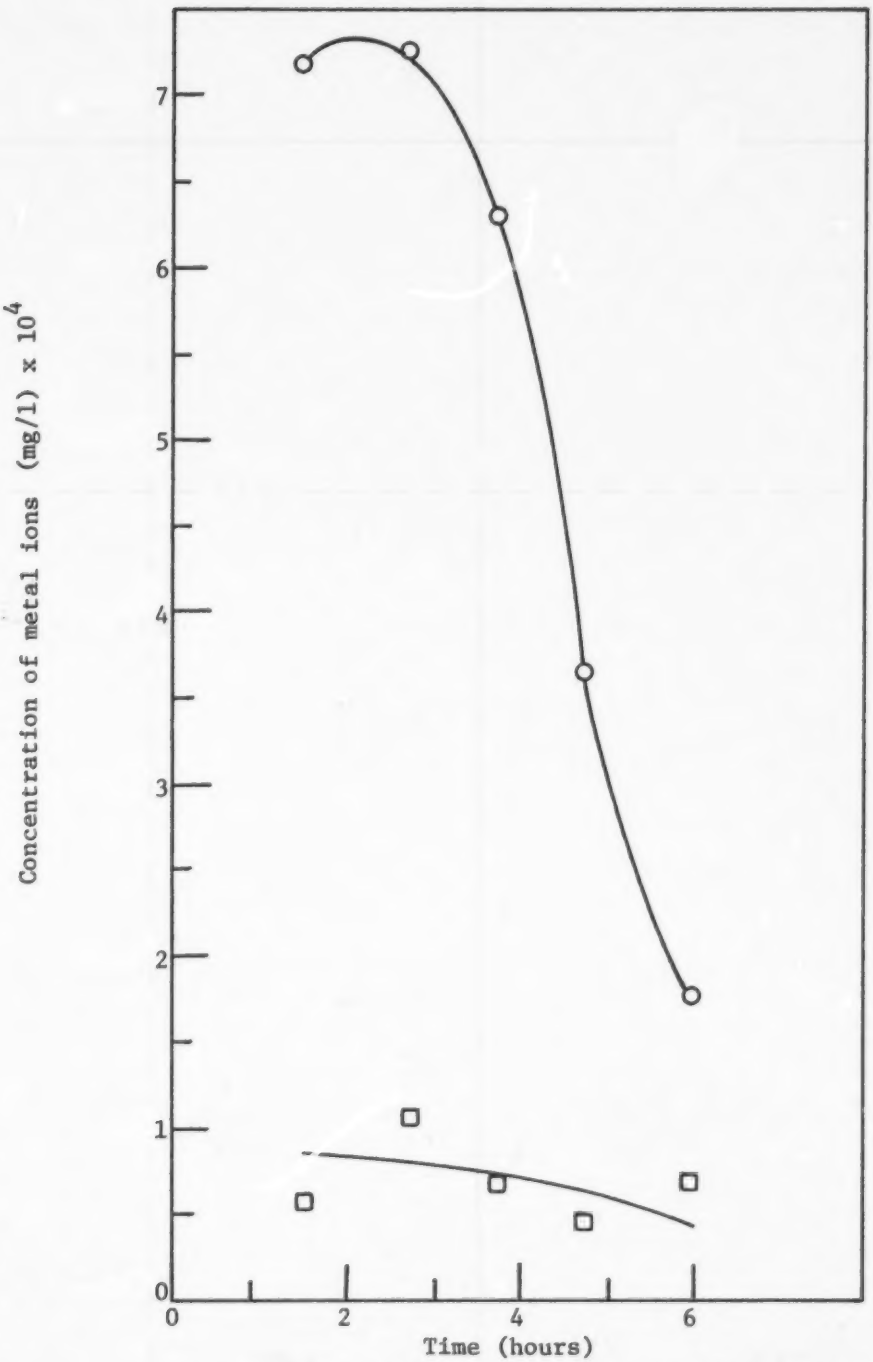

FIGURE 20. ELECTRODIALYSIS TREATMENT OF TIN FLUOBORATE RINSE-WATER, PRODUCT CATION CONCENTRATION

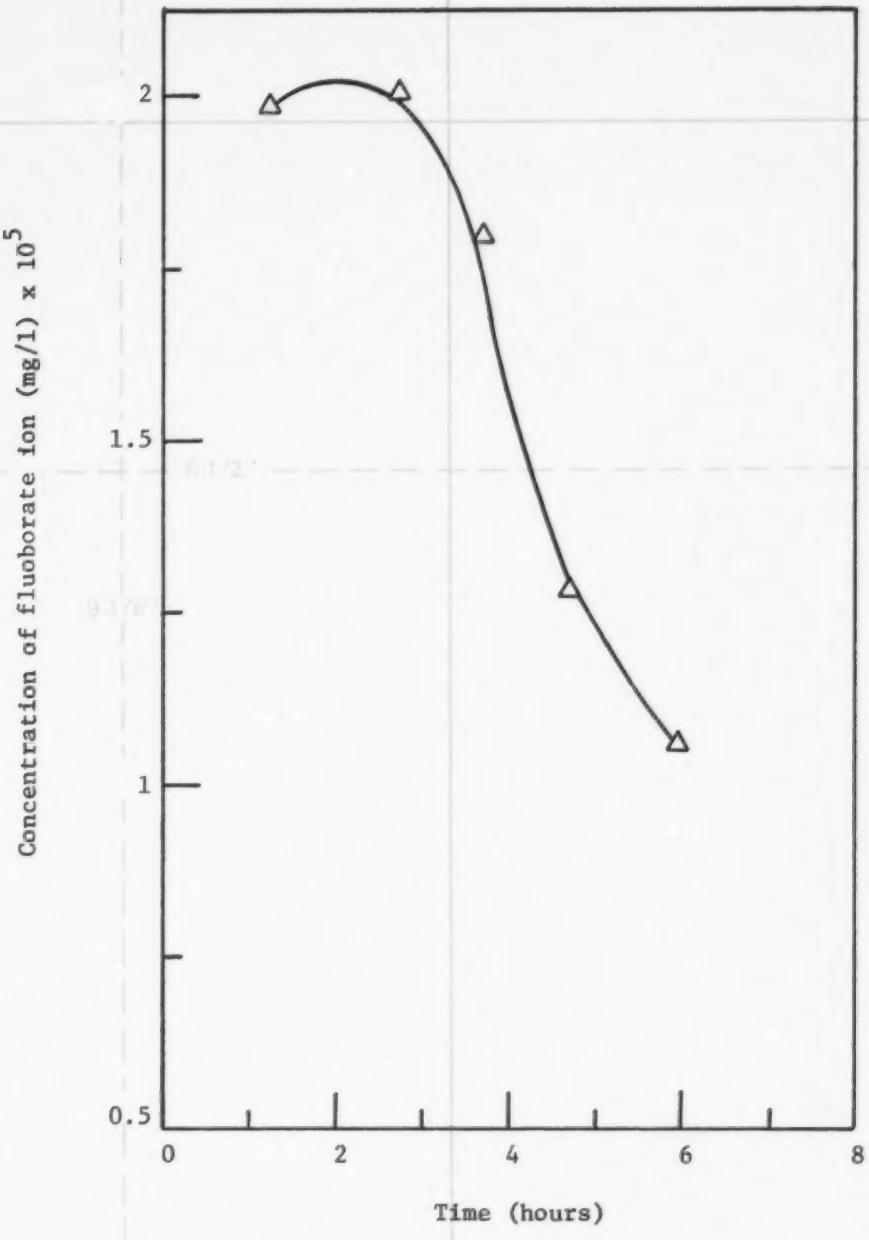

FIGURE 21. ELECTRODIALYSIS TREATMENT OF TIN FLUOBORATE RINSE-WATER, PRODUCT ANION CONCENTRATION

TABLE 5. Changes in Percent Stannous Cation in the Feed and Product with Time During the Electrodialysis Treatment of Tin Fluoborate Rinse-Water

Time (hours)	$\%Sn^{+2}$ feed	$\%Sn^{+2}$ product
0	83	
0.5	83	85
1.5	70	86
2.75	67	87
3.75	45	89
4.75	39	89
6.00	23	72

feed. After eight hours of operation, the stannous ion is reduced from about 275 mg/1 to below 5 mg/1, whereas, the stannic ion concentration in the feed was reduced from about 185 mg/1 to only about 165 mg/1 (see Figure 22). Reductions in the lead ion are comparable to the stannous ion. The lead ion concentration in the feed was reduced from about 190 mg/1 to below 5 mg/1.

Significant reductions in the concentration of fluoborate ion in the feed was also observed. During eight hours of operation, the fluoborate ion was reduced from 1920 mg/1 to about 220 mg/1 (see Figure 23). This reduction represents a removal of 90 percent of the fluoborate ion in the feed. Since the stannous ion is again observed to be removed at a much faster rate from the feed than the stannic ion, the concentration of stannous ion in the product should be significantly higher than the stannic.

Analysis of the initial product collected after the first hour of operation reveals the stannous ion concentration to be about 1300 mg/1 whereas, the stannic ion is found to be only 1800 mg/1 (see Figure 24). A 50 fold increase in the stannous ion concentration in the product is achieved over that originally present in the feed. The increase in the stannic ion concentration in the product represents only a 10 fold increase over that originally present in the feed. This is the same increase as encountered in the treatment of the tin fluoborate rinse. This greater rate of removal of the stannous ion produces a product where most of the total tin is in the form of stannous ion. The stannous ion in the product averages above 80 percent even though the percent stannous ion in the initial feed is only 62 percent (see Table 6).

Analysis for the lead ion in the products reveals that its concentration is comparable to that found for the stannous ion (see Figure 24). These

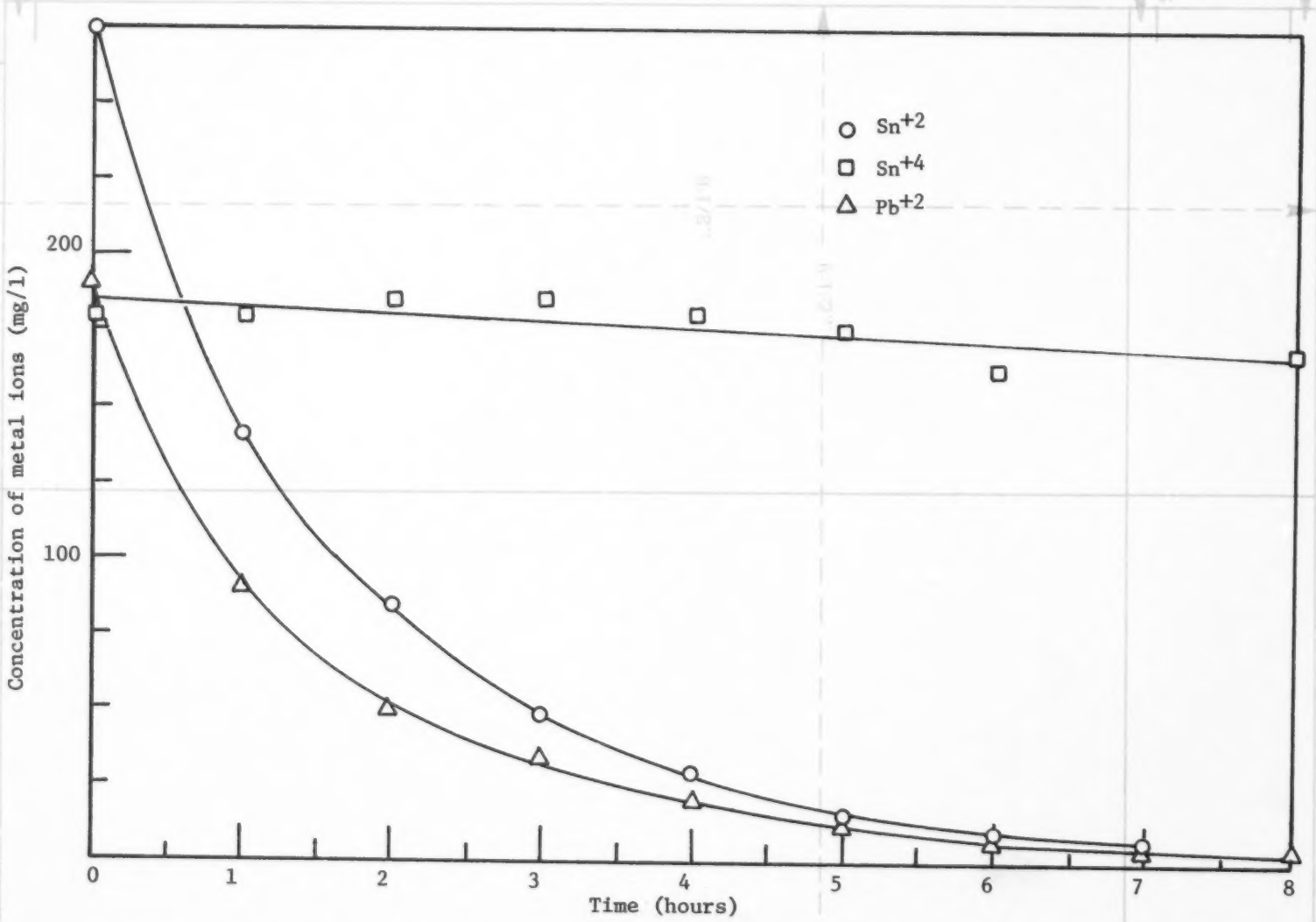

FIGURE 22. ELECTRODIALYSIS TREATMENT OF SOLDER FLUOBORATE RINSE-WATER, FEED CATION CONCENTRATION

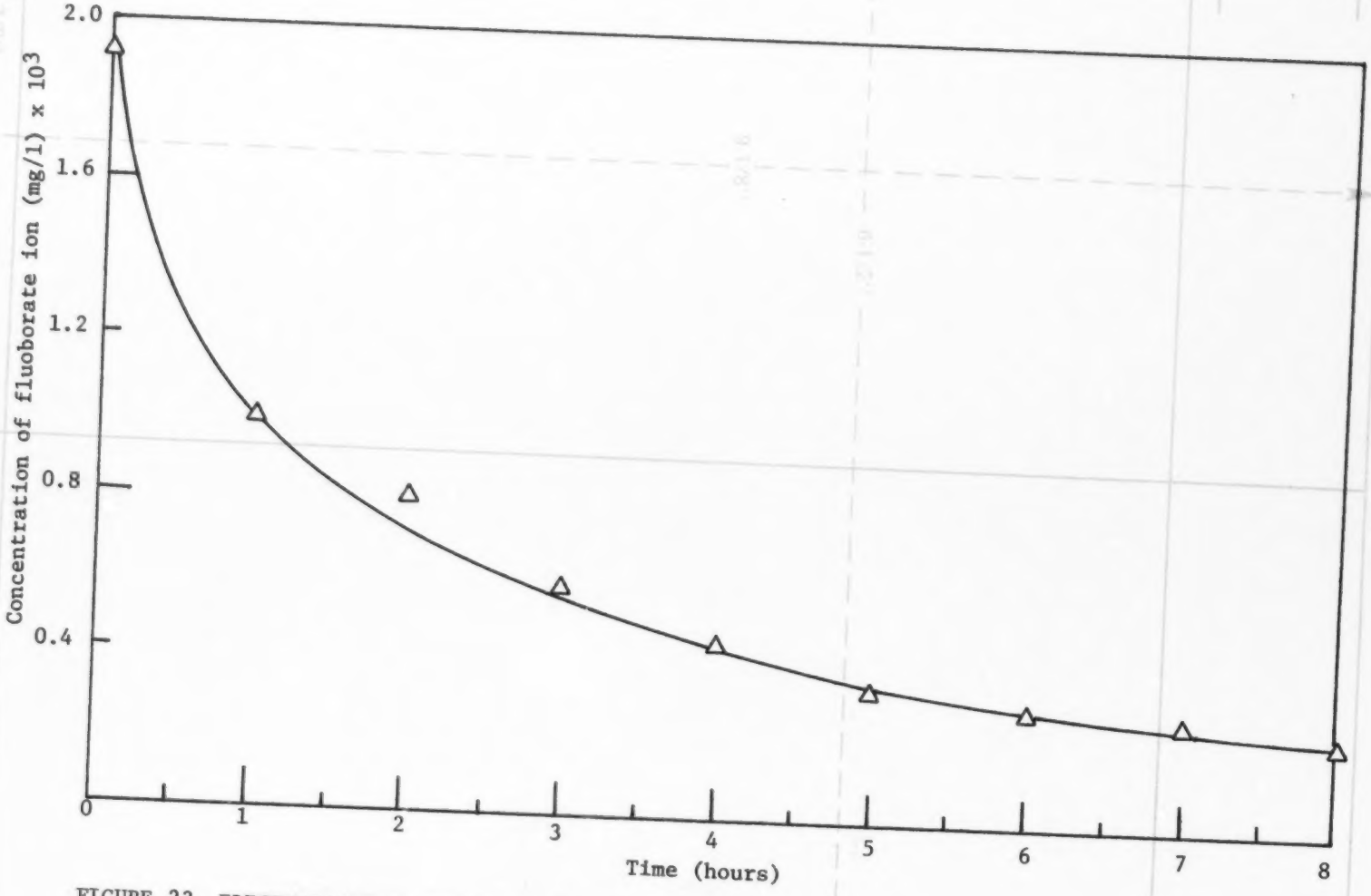

FIGURE 23. ELECTRODIALYSIS TREATMENT OF SOLDER FLUOBORATE RINSE-WATER, FEED ANION CONCENTRATION

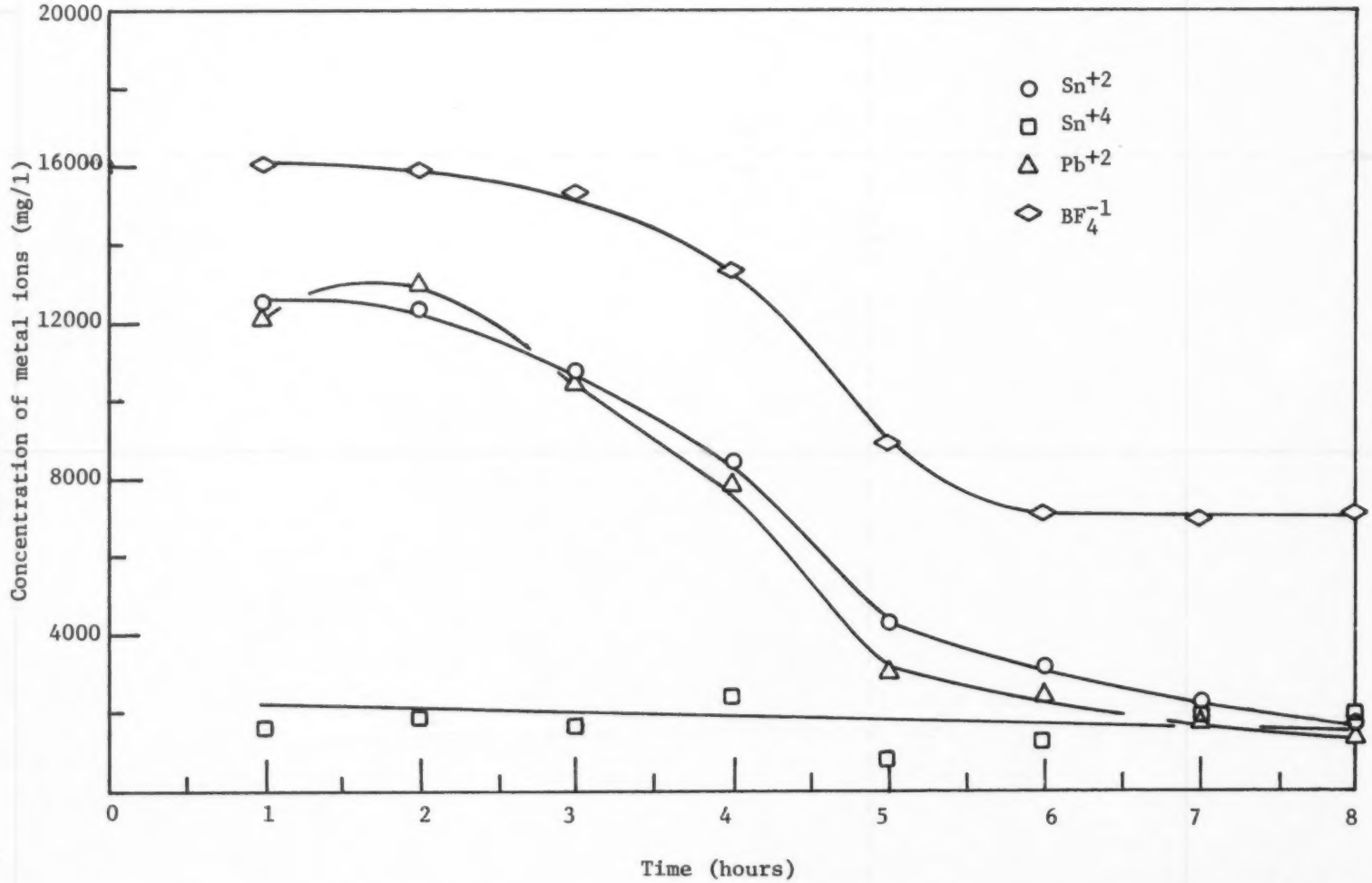

FIGURE 24. ELECTRODIALYSIS TREATMENT OF SOLDER FLUOBORATE RINSE-WATER, PRODUCT ION CONCENTRATION

results are expected since the removal of lead from the solder rinse-water feed as a function of time is comparable to that achieved with the stannous ion.

The fluoborate ion concentration in the product collected within the first hour of operation was found to be about 16,000 mg/1. This represents only a 10 fold increase in the fluoborate ion found in the product over that present in the initial feed. Treatment of the tin fluoborate rinse-water resulted in a 30 fold increase in the concentration of fluoborate anion in product over that found in the feed. The reason for smaller fluoborate anion concentration effect obtained in the product from the treatment of the solder rinse-water is not clear at this time.

The electrodialysis treatment of approximately 114 liters of solder rinse-water over a period of eight hours produced roughly 3.2 liters of product. This amounts to a volume ratio of product to feed of about 1:36. The concentration of stannous ion, stannic ion, lead ion and fluoborate ion in this product was found to be 6.5 gm/1, 0.6 gm/1, 5.9 gm/1 and 11 gm/1, respectively. The concentrations of stannous ion and lead ion in the product are about half of the concentrations of stannous and lead ions commonly used in the solder plating bath. The concentrations of fluoborate ions in the product represents about one 40th of the fluoborate ion used in the plating baths. These results represent a 97 percent recovery of stannous ion and lead ion, 88 percent of the fluoborate ion and 11 percent of the stannic ion.

Treatment of Copper Fluoborate Rinse-Waters

The electrodialysis treatment of the copper fluoborate rinse- waters were carried out under the same experimental conditions as the tin and solder rinse-waters. The copper ion in the feed was reduced from initially

TABLE 6. Changes in Percent Stannous Ion in Feed and Product with Time During Electrodialysis Treatment of Solder Fluoborate Rinse-Water

Time (hours)	$\%Sn^{+2}$ feed	$\%Sn^{+2}$ product
0	62	
1	44	89
3	32	86
4	15	79
5	8	83
6	6	70

2500 mg/1 to less than 40 mg/1 in approximately three hours (see Figure 25). This represents about a 97 percent reduction in copper ion concentration in the feed in three hours. In comparison, a 97 percent reduction in the stannous ion in the tin fluoborate rinse-water and the solder rinse-water required 6 hours and 8 hours, respectively. A 97 percent reduction in the solder rinse-water feed also required 8 hours.

The greatest reduction in the fluoborate ion concentration in the treatment of the copper fluoborate rinse feed was encountered in the initial four hours of operation. The concentration of the fluoborate ion in the feed was reduced from 7500 mg/1 to 650 mg/1 during this period (see Figure 26). This reduction amounts to 90 percent removal of the fluoborate ion in the feed. In comparison, the electrodialysis treatment of both the tin and solder fluoborate rinse-waters required 8 hours to achieve the same removal percentages. Apparently, the presence of stannic ion in the feed of the tin and solder rinse-water which is removed at a much slower rate than the stannous and lead ions may inhibit the removal of the fluoborate ion.

The analysis of the products collected from the electrodialysis of copper fluoborate rinse-water after about 1½ hours of operation showed a 20 fold increase in cupric and fluoborate ion over their initial concentration. The cupric and fluoborate ion in the product was about 53,000 mg/1 and 160,000 mg/1, respectively after 1½ hours of operation (see Figure 27).

In comparison, the initial stannous and fluoborate ion product concentration collected from the electrodialysis of the tin fluoborate rinse-water showed a 30 fold increase over that present in the initial feed. The initial stannous and lead ion product concentration from electrodialysis of the solder bath rinse-water showed about a 50 fold increase whereas the initial

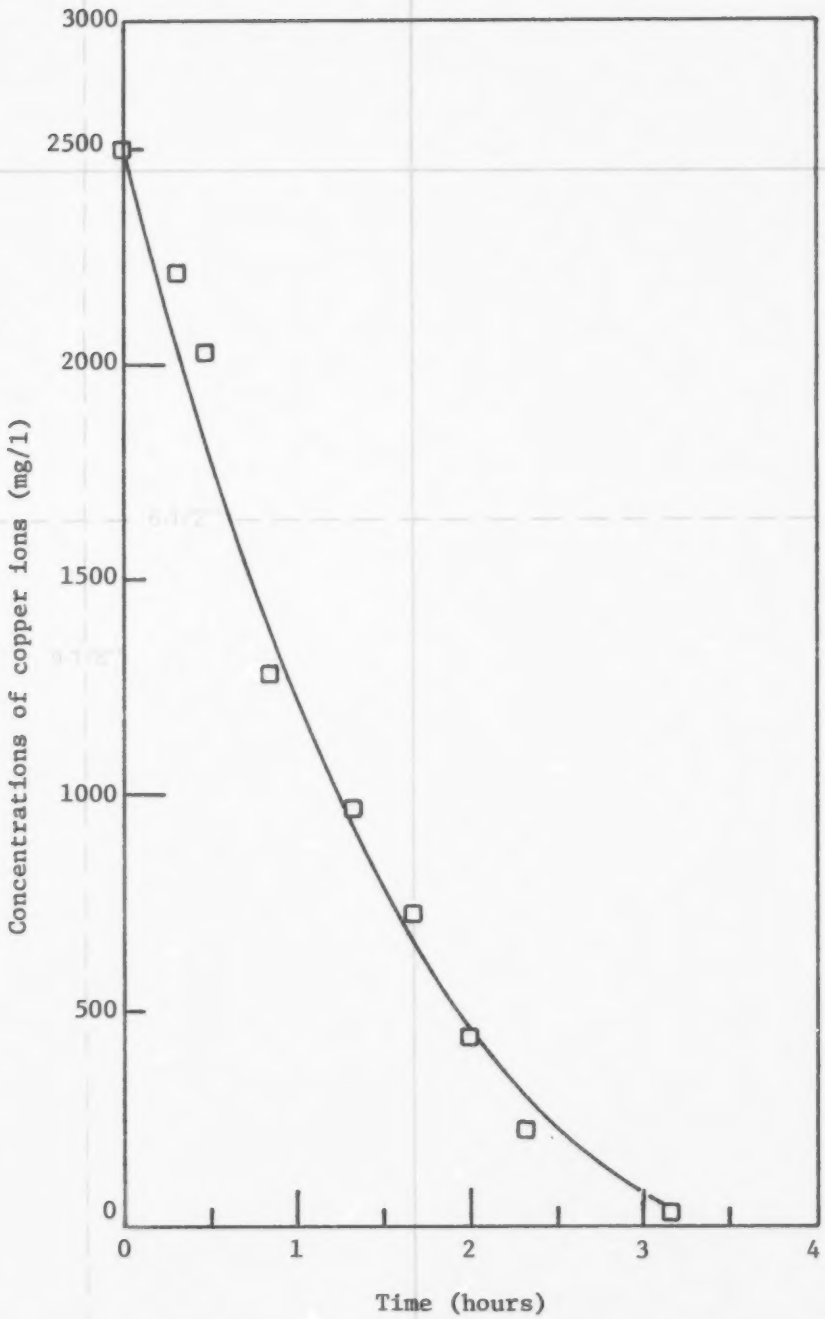

FIGURE 25. ELECTRODIALYSIS TREATMENT OF COPPER FLUOBORATE RINSE-WATER, FEED ANION CONCENTRATION

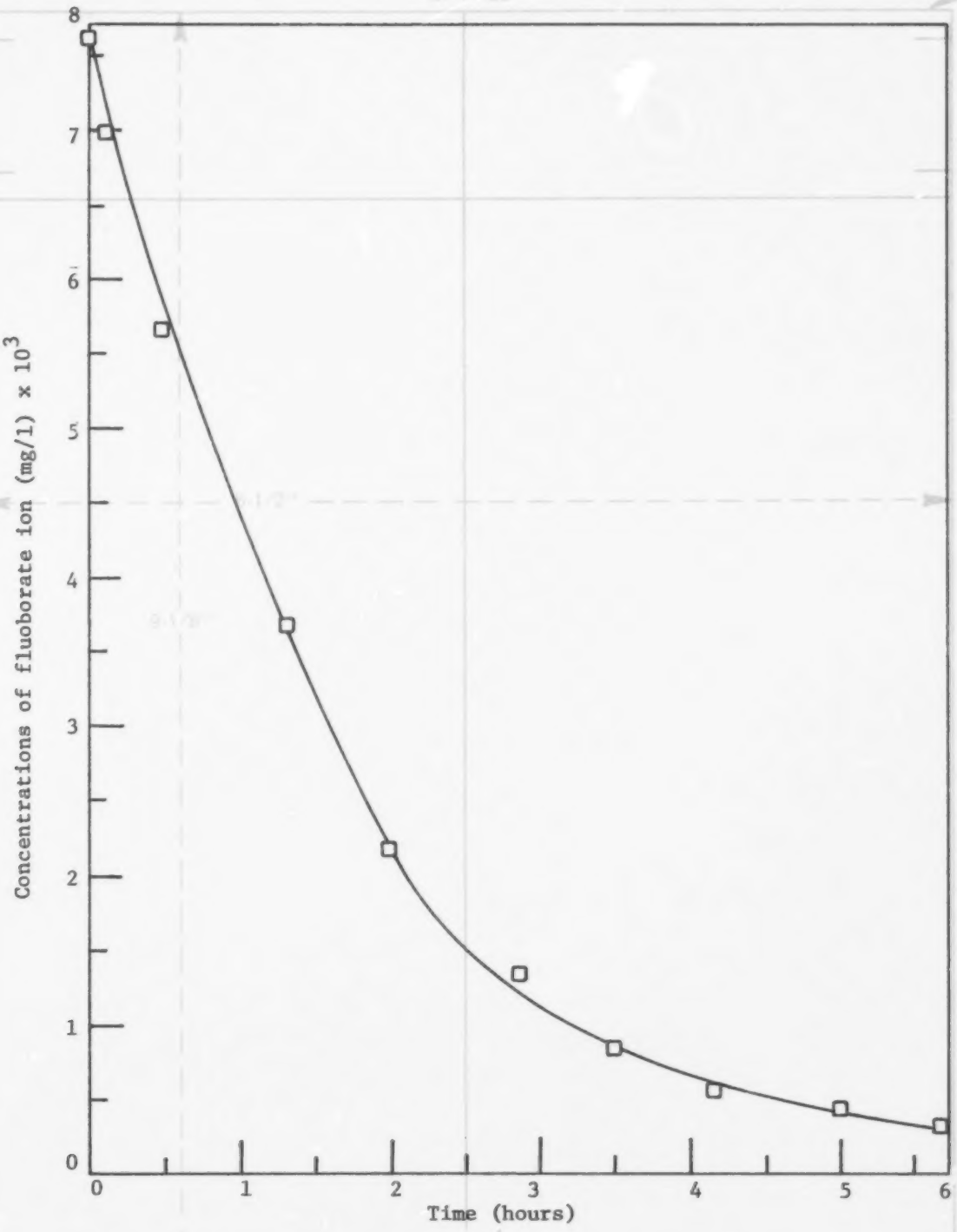

FIGURE 26. ELECTRODIALYSIS TREATMENT OF COPPER FLUOBORATE RINSE-WATER, FEED ANION CONCENTRATION

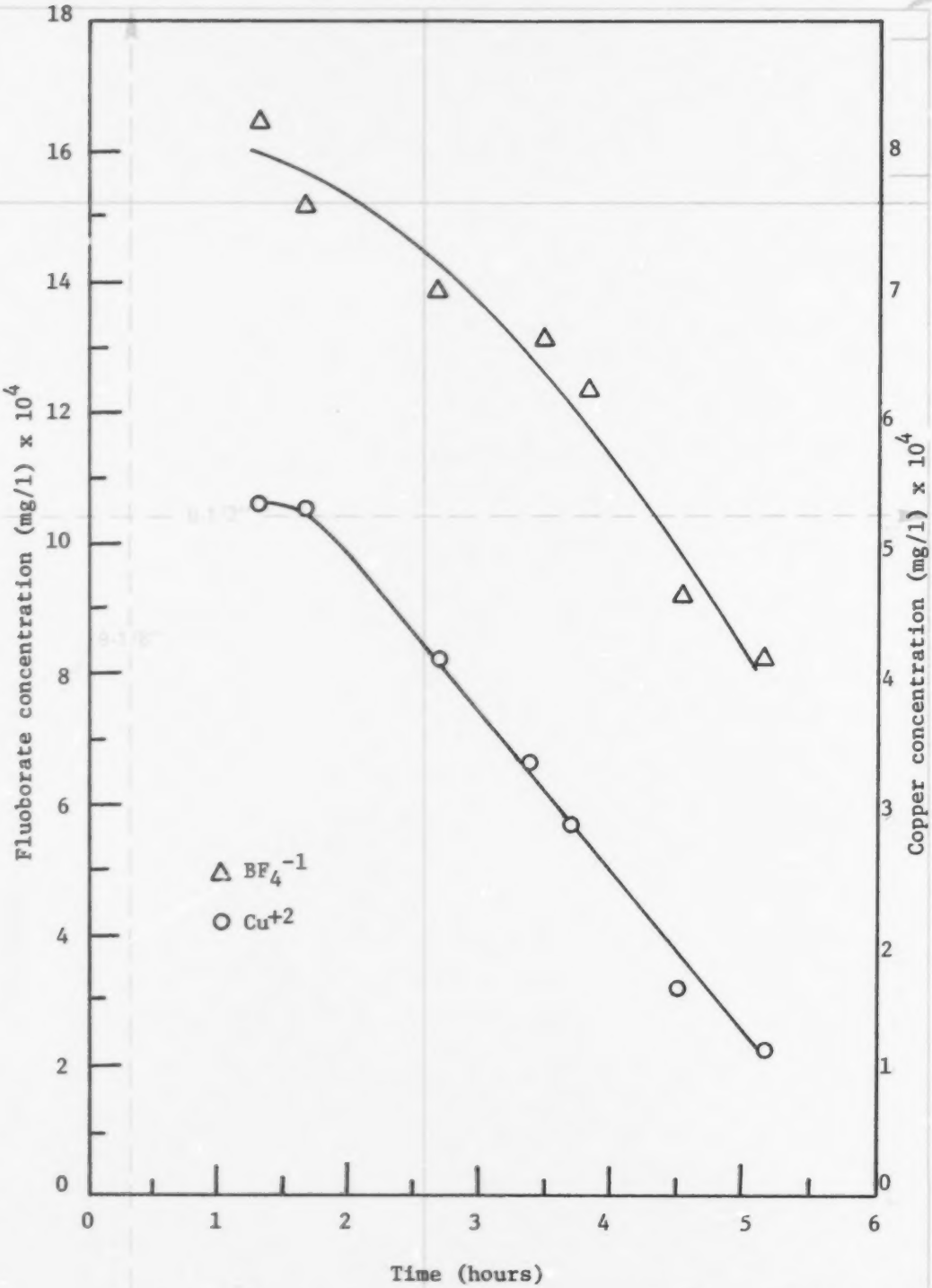

FIGURE 27. ELECTRODIALYSIS TREATMENT OF COPPER FLUOBORATE RINSE-WATER, PRODUCT ION CONCENTRATION

fluoborate ion product concentration showed only a 10 fold increase.

The electrodialysis of the copper fluoborate rinse-water over a period of slightly less than 6 hours produced roughly 7 liters of product. This amounts to a volume ratio of product to feed of 1:17. The concentration of cupric ion and fluoborate ion present in this product was found to be about 40 gm/l and 120 gm/l respectively. The cupric concentration in the product is about 3 times more concentrated than plating bath strength and the fluoborate ion concentration is about one-third that generally used in a copper plating bath.

Rates of Mass Transfer

The results of the treatment of the fluoborate plating bath rinse-waters indicate that the rate of mass transfer of the ions across a square centimeter of membrane surface from the feed to the concentrate is dependent upon the cations in the rinse-waters and plating bath rinse-water that is being treated. The rate of mass transport across one square centimeter of membrane surface for the stannous ions from both the tin and solder rinse-water feed, respectively are comparable (see Table 7). The lead ion in the solder rinse-water feed is also removed at approximately the same rate (1.4 mg/hr. cm^2) as the stannous ion (1.7 mg/hr. cm^2, 1.9 mg/hr. cm^2). The stannic ion on the other hand shows a mass transport rate that is some 10 times slower than the rates obtained with the stannous and lead ions. These results cannot be explained at this time because the charge on the cation does not appear to influence the mass rate of transfer. The stannic cations with a +4 charge would be expected to move across the membrane at a greater rate than a cation with a +2 charge. Yet the copper ion has the same +2 charge as the stannous and lead ions, but exhibits a 20 times faster rate of

transport (41 mg/hr. cm^2) then either the stannous or lead ions.

The rate of mass transfer of the fluoborate anion also appears to be dependent upon the plating rinse-water. The rate of mass transport exhibited by the fluoborate anion in the copper bath rinse-water is significantly higher than that encountered in either the tin or solder bath rinse-water (see Table 7). The rate of mass transport is 94 mg/hr. cm^2 in the copper rinse-water following in decreasing order by 28 mg/hr. cm^2 and 12 mg/hr. cm^2 in the tin and solder rinse-water, respectively. The difference in mass rate of transport between the fluoborate anion in the treatment of the tin and solder rinse-waters cannot be explained at this time. Since the rate of mass transport for the stannous and stannic ions between the tin and solder rinse-waters are comparable, one would expect the rate of mass transport for the fluoborate anion to be similar.

Analysis of Electrolyte

The electrolysis or hydrolysis of the electrolyte as evidenced by changes of pH and fluoborate concentration was not observed. Both the pH and fluoborate concentration in the electrolyte remained constant during the electrodialysis treatment of the tin, solder and copper fluoborate rinse-waters.

TABLE 7. Rate of Mass Transport of Cations and Fluoborate from the Tin, Solder, Copper Fluoborate Rinse-Waters

Ions	Plating Bath Rinse-Waters Rate of Mass Transport (mg/hr. cm^2) Tin fluoborate	Solder fluoborate	Copper fluoborate
Sn^{+2}	1.7	1.9	
Sn^{+4}	.19	.14	
Pb^{+2}		1.4	
Cu^{+2}			41
BF_4^-	28	12	94

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